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16. ABSTRACT The document summarizes or contains an abstract of each presentation made at the EPA-sponsored symposium, October 26-30, 1981, in Denver, CO. The symposium provided a forum for the exchange of ideas and for discussion of environmentally related information on coal gasification and liquefaction. Process developers and users, research scientists, and government officials reported on results achieved from research projects, synfuels process development, interagency programs, control technology evaluation, and regulatory actions. The program included sessions on environmental source test and evaluation results for gasification, indirect liquefaction, and direct liquefaction processes, and water-, air-solid-waste-, multimedia-, and product-related environmental considerations. Approximately 215 participants attended the 5-day symposium.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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Coal Gasification	Stationary Sources	13H
Coal	Synthetic Fuels	08G,21D
Liquefaction	Fuel Conversion	07D
Manufactured Gas		

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A Symposium on Coal-Based Synfuels
(October 26-30, 1981)

F. A. Ayer and N. S. Jones, Compilers

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PREFACE

These proceedings for the symposium on "Environmental Aspects of Fuel Conversion Technology-VI" constitute the final report submitted to the Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency, (EPA/IERL-RTP), Research Triangle Park, NC. The symposium was conducted in Denver, Colorado, October 26-30, 1981.

This symposium provided a forum for the exchange of ideas and for discussion on environmentally related information on coal gasification and liquefaction. The program included sessions on environmental source test and evaluation results for gasification and indirect liquefaction, and for direct liquefaction, on water-related environmental considerations, on solid waste-related environmental considerations, on multimedia environmental considerations, and on product-related environmental considerations.

Process developers and users, research scientists, and state and federal officials participated in the symposium, the sixth to be conducted on this subject by IERL-RTP since 1974.

N. Dean Smith, Gasification and Indirect Liquefaction Branch, EPA/IERL, Research Triangle Park, NC, was the Project Officer and the Technical Chairman. William J. Rhodes, Synfuels Technical Coordinator for EPA/IERL-RTP, was General Chairman.

Franklin A. Ayer, Manager, and N. Stuart Jones, Analyst, Technology and Resource Management Department, Center for Technology Applications, Research Triangle Institute, Research Triangle Park, NC, were symposium coordinators and compilers of the proceedings.

In these proceedings, the title of each paper that has resulted from an EPA-funded project is marked with a (†) to indicate that it has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

The absence of a (†) in the title of a paper in these proceedings indicates that the paper is not the result of EPA-funded work and, therefore, its contents do not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

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Session I: ENVIRONMENTAL SOURCE TEST AND EVALUATION RESULTS

Part A: Gasification and Indirect Liquefaction

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U.S. Environmental Protection Agency
Research Triangle Park, NC

Cochairman: William C. Yee
Tennessee Valley Authority
Knoxville, TN

PB83-128199

CHARACTERIZATION OF PROCESS LIQUIDS AND ORGANIC † CONDENSATES FROM THE LURGI COAL GASIFICATION PLANT AT KOSOVO, YUGOSLAVIA

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ABSTRACT

Process liquids and gaseous stream condensates from the Lurgi Coal Gasification plant at Kosovo were characterized to define their organic composition. Samples of entrained liquids and condensates were collected during Phase II of the Kosovo source test that was described at the preceeding Synfuel Symposium. These samples were characterized by Liquid Chromatographic fractionation using EPA's protocol for a Level I source assessment. In addition, GC-MS analyses were performed on key samples to quantify their levels of potentially hazardous PNA's, and GC with selective detection was used to characterize sulfur and nitrogen bearing species.

This presentation will provide a discussion of the analytical results and of the impact that these condensates have on the plant's discharge stream severity. It will also include a comparison of the composition of liquids from the Lurgi process with the compositions of liquids from other processes.

INTRODUCTION

Process liquids, gas stream condensates and solid wastes from the Kosovo Coal Gasification Plant were characterized to determine their organic composition. Samples were taken from fourteen gas streams, plus five liquid and two solid phase streams during Phase II of the source test that was sponsored jointly by the United States Environmental Protection Agency and the Government of Yugoslavia. Sampling and analyses were conducted as a cooperative effort by American and Yugoslav scientists (1, 2).

The 21 streams selected for organic characterization are identified in Table 1. These streams provided a representative cross section of the Lurgi technology that is used at Kosovo. The locations of these streams are included in the plant's description.

TABLE 1. ANALYSES PERFORMED ON KOSOVO GAS STREAM CONDENSATES, PROCESS LIQUID AND SOLID WASTES

Stream	Analyses						
	Particulate Determination	TCO	Grav	LC	GC Sulfur	GC Nitrogen	GCMS PNA'S
Gas Stream							
Fleissner Autoclave Vent	x	x	x	x			
LP Coal Lock Vent	x	x	x	x	x	x	x
HP Coal Lock Vent	x	x	x	x	x	x	
Start-up Vent	x	x	x	x			x
H_2S-Rich Waste Gas		x	x	x		x	x
CO_2-Rich Waste Gas		x	x				x
Crude Product Gas		x	x			x	
Tar Tank Vent		x	x	x		x	x
Medium-Oil Tank Vent		x	x	x		x	x
Tar Separation Waste Gas	x	x	x	x		x	
Phenolic Water Tank Vent		x	x	x		x	x
Ammonia Stripper Vent		x	x	x	x	x	x
Naphtha Storage Tank Vent		x	x	x			x
Waste Gasses to Flare	x	x	x				
Other Streams							
Fleissner Condensate			x				
Gasifier Ash			x				
Heavy Tar	x	x	x				
Phenolic Water	x	x	x		⊕	⊕	⊕
Tar		x	x	x	⊕	⊕	⊕
Medium Oil		x	x	x	+	+	⊕
Naphtha		x			⊕		⊕

x - analyzed in Yugoslavia.
+ - analyzed in US using grab samples taken at random.
⊕ - Data not included in this report, but included in Reference 2.

The gasification plant consists of nine operational units as illustrated in Figure 1. The plant consumes dried lignite and produces two primary products (a medium Btu fuel gas and hydrogen) plus four by-products (tar, medium oil, naphtha and crude phenol). The plant's operation is as follows: run of the mine coal is dried in steam autoclaves by the Fleissner process and then sized to select particles suitable for the Lurgi gasifiers (dp = 6 - 60 mm). The dried coal is fed through a pressure lock system (Coal Lock Vents) to a 3.5 M diameter Lurgi gasifier where it is reacted with steam at 2.5 MP (25 atm) pressure to produce a crude gas which is quenched, cooled and then cleaned by the Rectisol process prior to its transport to the utilization site. As the hot gas is quenched and cooled, organic matter consisting of phenols, tars and oils are removed with quench liquor and hot gas condensate. In the gas cleaning operation, condensable organics are removed from the cooled gas by refrigeration after which the acid-gases (H_2S and CO_2) are removed by sorption in cold methanol. The acid-gas rich methanol is regenerated by depressurization and heating, releasing H_2S-rich Waste Gas which is flared and CO_2-Rich Waste Gas which is vented into the atmosphere.

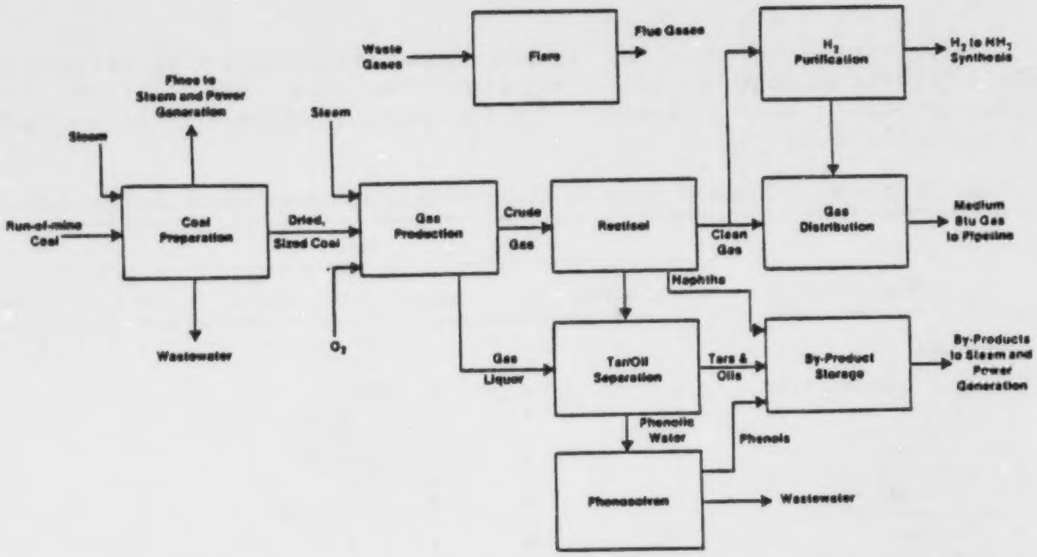

Waste Gases
Flare
Flue Gases
H$_2$ Purification
H$_2$ to NH$_3$ Synthesis
Fines to Steam and Power Generation
Steam
Steam
Run-of-mine Coal
Coal Preparation
Dried, Sized Coal
Gas Production
Crude Gas
Rectisol
Clean Gas
Gas Distribution
Medium Btu Gas to Pipeline
Wastewater
O$_2$
Naphtha
Gas Liquor
Tar/Oil Separation
Tars & Oils
By-Product Storage
By-Products to Steam and Power Generation
Phenolic Water
Phenols
Phenosolvan
Wastewater

Figure 1. Simplifed Flow Diagram of the Kosovo Coal Gasification Plant.

Tar, heavy tar and medium oil are each separated from their aqueous phase by decantation after which the combined waters are depressurized (Phenolic Water Tank) then stripped to remove ammonia (Ammonia Stripper Vent) and then extracted with disopropyl ether to remove extractable organics (Crude Phenol) prior to disposal.

EXPERIMENTAL

The sample characterization program consisted of a combination of the following methods: gas and liquid chromatographic fractionation using EPA's protocol for a Level 1 Environmental Source Assessment to determine the mass distributions of volatile and non-volatile organics; gas chromatographic analyses with both universal and selective GC detections to characterize organics; and GC-MS analysis to quantify certain potentially hazardous polynuclear aromatic compounds. The distributions of volatile and non-volatile organics were determined by the EPA protocol as Total Chromatographable Organics (TCO) and Gravimetrically Determined Organics (Grav) respectively (3).

Condensable organics were collected from gaseous streams with a sampling train that consisted of an entrainment separator, an ice cooled condenser, and a resin filled absorber in series. In some cases, sample collections were made in conjunction with a particulate measurement for which the entrained and condensed liquids were combined and then divided equally for the particulate determination and the organic characterization. In most cases, collections were made specifically for the organic characterization. All samples were refrigerated during the storage period between collection and work-up for analysis.

Sorbed vapors from the respective streams were recovered from their collection resin by soxhlet extraction with methylene chloride and were combined with the organic extracts from their stream's condensates prior to analysis by the EPA protocol for TCO. The strategy followed for these determinations is illustrated in Figure 2.

To supplement the information provided by the TCO and Grav determinations, the extracts from selected streams (Table 1) were analyzed by gas chromatography with element specific detection to obtain profiles of the sulfur and nitrogen-containing species.

Polynuclear aromatics (PNA's) were determined on several streams by GC-MS. A liquid crystal GC column was used to isolate Benzo(a)pyrene from other isomeric PNA's.

The streams sampled and the analyses performed are summarized in Table 1.

RESULTS AND DISCUSSION

The concentrations of organics in the thirteen major gaseous streams of the Kosovo gasification plant (shown in Table 2) indicate that the phenolic water tank discharges the highest concentration of organics in the Kosovo plant (1.2×10^5 mg/m^3) and that a major portion (92%) of the emission is due to TCO. The TCO value obtained from this measurement is a factor of five higher than the level indicated by light aromatic concentrations that were determined during the Phase II test. The significant difference between these two values is not explained. The discharge from the ammonia stripper vent also contains a high concentration of organics but in this stream the mass concentrations of the TCO hereafter called volatile organics (VO) and Grav hereafter called non-volatile organics (NVO) are about equal (57% volatiles). Excluding the two high concentration streams, the average concentration of combined organics in tested streams was 5,800 mg/m^3 with most values falling in a range between 1,000 and 20,000 mg/m^3. As expected, the lowest concentration of combined organics was found in the CO_2-rich waste gas. The value obtained in this stream for non-volatile organics may not be significant since it is based on a single determination and probably is within the noise level of the analytical method. A more accurate measurement is required to establish, definitively, the level of condensable organics in this stream.

A comparison of the concentration levels of VO's with the concentrations of light aromatics, as determined during Phase II of the source test, is shown in Table 3. The light aromatic values shown are the sum of phenol plus C_1 and C_2 alkyl aromatics. These light aromatics are included in the volatile organics determination and appear to represent a significant portion (30 to 60%) of the materials determined as VO. In cases where the concentrations of light aromatics are greater than the concentration of VO, it is not known whether the difference is due to variations in the stream's composition or to analytical error. However, the VO and light aromatic concentration values, when considered together, provide a reasonable indication of the quantities of volatile organics in the respective streams.

A similar comparison is made in Table 4 between the concentration values of NVO and the Tar and Oil (T&O) values that were reported for particulates in several streams. In this comparison, most values fall within a factor of 2

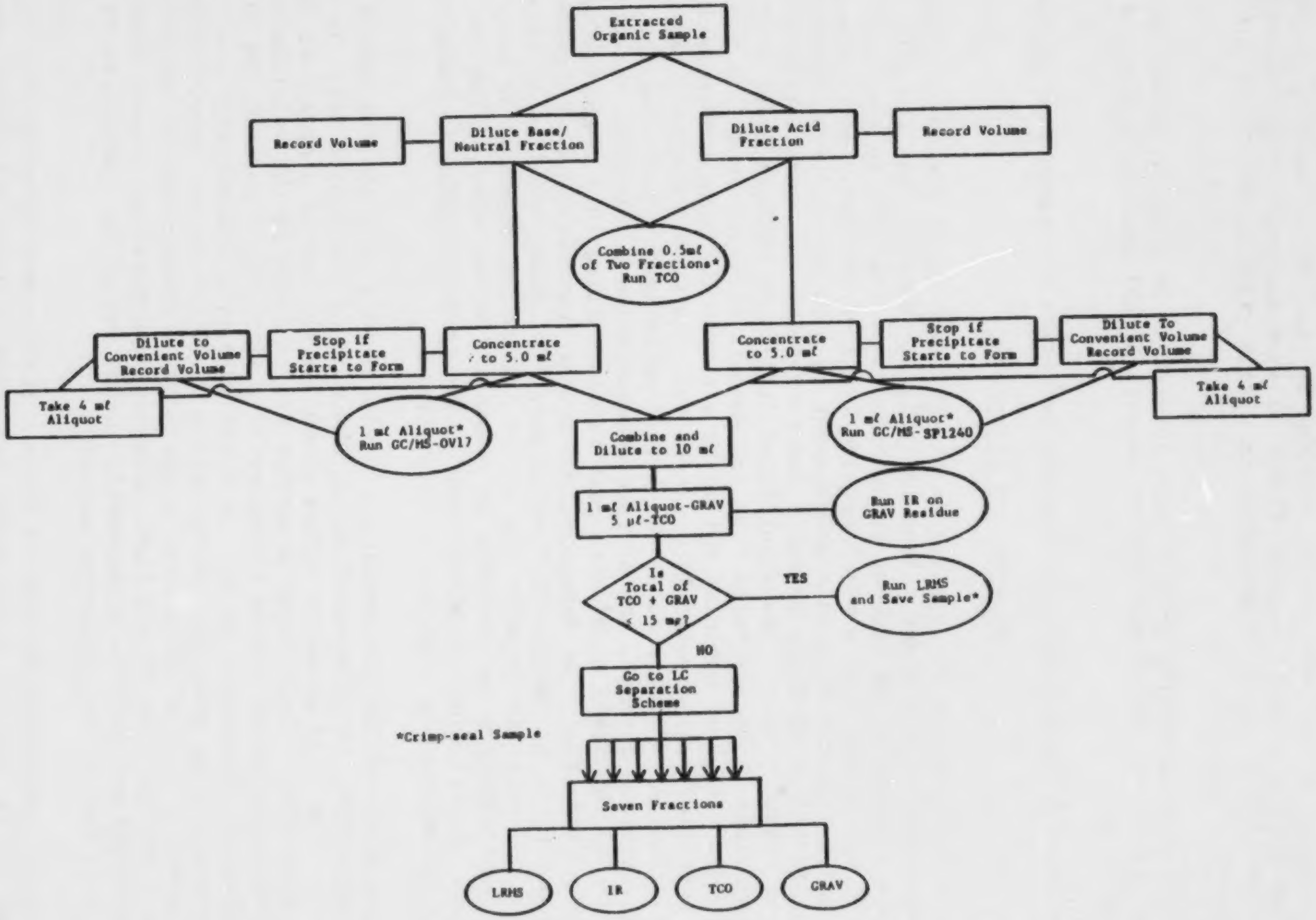

Extracted Organic Sample
Dilute Base/ Neutral Fraction
Dilute Acid Fraction
Record Volume
Record Volume
Combine 0.5mℓ of Two Fractions* Run TCO
Dilute to Convenient Volume Record Volume
Stop if Precipitate Starts to Form
Concentrate to 5.0 mℓ
Concentrate to 5.0 mℓ
Stop if Precipitate Starts to Form
Dilute To Convenient Volume Record Volume
Take 4 mℓ Aliquot
1 mℓ Aliquot* Run GC/MS-OV17
Combine and Dilute to 10 mℓ
1 mℓ Aliquot* Run GC/MS-SP1240
Take 4 mℓ Aliquot
1 mℓ Aliquot-GRAV 5 μℓ-TCO
Run IR on GRAV Residue
Is Total of TCO + GRAV < 15 mg?
YES
Run LRMS and Save Sample*
NO
Go to LC Separation Scheme
*Crimp-seal Sample
Seven Fractions
LRMS
IR
TCO
GRAV

Figure 2. Strategy Followed for the Characterization of Kosovo Organics.

TABLE 2. CONCENTRATIONS OF VOLATILE AND NONVOLATILE ORGANICS IN KOSOVO PLANT GAS STREAM CONDENSATES

	mg/m^3				
Source	Volatile Organics[1] (TCO)	Non-Volatile Organics[2] (Grav)	Total Organics[3]	% Volatile Organics	% Non-Volatile Organics
Fleissner Autoclave Vent	306	807	1,113	27	73
LP Coal Lock Vent	3,732	4,007	7,739	48	52
HP Coal Lock Vent	1,622	1,250	2,872	57	43
Start-up Vent	2,670	7,053	(9,723)	27	73
H_2S-Rich Waste Gas**	40	90	130	31	69
CO_2-Rich Waste Gas	5	9	14	36	64
Tar Tank Vent	10,785	3,628	14,412	75	25
Medium Oil Tank Vent	19,921	1,197	21,118	94	6
Tar Separation Waste Gas	2,335	967	3,302	71	29
Phenolic Water Tank Vent	115,012	9,869	124,881	92	8
Ammonia Stripper Vent	56,167	43,051	99,218	57	43
Naphtha Storage Tank Vent	5,089	499	5,588	91	9
Combined Gas to Flare	312	290	602	52	48

[1] Volatile organics were determined as total chromatographable organics (TCO's) using EPA's Protocol which is based on a gas chromatographic determination of substances eluting in the range of C_7 to C_{16} hydrocarbons representing a boiling range between 100 and 300°C.

[2] Non-volatile organics were determined gravimetrically using EPA's Protocol for "Grav" which includes all substances retained from a 24-hour ambient evaporation. The Protocol may allow the same mid-range volatiles to be included in both determinations; consequently the total may be higher than the true value.

[3] These values are a summation of toluene, xylene, and phenol as determined during the Phase II test and are included for comparison.

**No XAD-2 value included.

TABLE 3. COMPARISON BETWEEN VOLATILE ORGANICS (TCO) AND SUMMED LIGHT AROMATICS (C_1 + C_2 ALKYL AROMATICS + PHENOL) AS DETERMINED DURING PHASE II OF THE KOSOVO SOURCE TEST

Source	Volatile Organics	Σ Light Aromatics
LP Coal Lock Vent	3,732	1,170
HP Coal Lock Vent	1,622	1,730
H_2S-Rich Waste Gas	40	30
CO_2-Rich Waste Gas	5	10
Tar Tank Vent	10,785	3,790
Medium Oil Tank	19,921	6,060
Tar Separation Waste Gas	2,335	5,190
Phenolic Water Tank	115,012	21,670*
Ammonia Stripper Vent	56,167	23,800
Naphtha Storage Tank	5,089	7,410

*Phenol value was calculated from its vapor pressure over a saturated aqueous solution at 65°C.

TABLE 4. COMPARISON BETWEEN ORGANICS COLLECTED BY PARTICULATE TRAIN AND THOSE COLLECTED VIA ORGANIC TRAIN

Source	Tar & Oil	Non-Volatile Organics	Total Organics Σ VO + NVO
Fleissner Autoclave Vent	534	808	1,114
LP Coal Lock Vent	7,920	4,007	7,739
HP Coal Lock Vent	953	1,634	3,753
Start-up Vent	9,800	7,051	9,721
Tar Separation Waste Gas	723	967	3,302

of each other (mean = 1.2 ± 0.5). As with the previous comparison, these results provide a reasonable indication of the level of non-volatile organics (Tars and Oil) which are transported by the respective streams.

The mass flow of combined organics in each stream is shown in Table 5. These results show that two streams (the start-up vent and the ammonia stripper vent) transport, by far, the greatest quantity of organic matter (98%). Either of these streams, when operating, transports more condensable organics than all of the other streams combined.

TABLE 5. MASS FLOW OF CONDENSABLE ORGANICS IN KOSOVO GASEOUS STREAMS

Source	Stream Flow m^3/hr	Mass Flow g/hr	% Non-Volatile
LP Coal Lock Vent	21	163	52
HP Coal Lock Vent	230	660	43
Start-up Vent	12,500	121,538	73
H_2S-Rich Waste Gas	3,600	468	69
CO_2-Rich Waste Gas	3,600	50	64
Tar Tank Vent	0.55	8	25
Medium Oil Tank Vent	1.7	36	6
Gar Separation Waste Gas	28	92	29
Phenolic Water Tank Vent	5.5	687	8
Ammonia Stripper Vent	260	25,797	43
Naphtha Storage Tank Vent	4.5	25	9

Since both the composition and the flow rate of the discharge from the start-up vent varies considerably over the start-up period, the values presented here may represent a worst-case; nevertheless, the discharge is significant because a large gasification complex having many gasifiers can be expected to have at least one gasifier in a start-up mode at all times. Under such conditions, the start-up stream could flow continuously.

The ammonia stripper vent, reported previously as the most environmentally significant stream in the Kosovo Plant (1), is also the major source of condensable organics. This stream is intermittent at Kosovo because the Phenosolvan plant is operated on demand, whereby phenolic water is accumulated in two large tanks and processed at a rate that is independent of the gas production rate. However, when the plant is operated at design capacity, continuous operation is necessary and the stripper vent is then a continuous discharge stream.

The phenolic water tank discharge contains the highest concentration of condensable organics, but because of its lower stream volume, its organic mass discharge rate is comparable to lower concentration but higher volume streams, e.g., the HP coal lock vent and the H_2S-rich waste gas stream.

The naphtha tank discharge which contained high concentrations of benzene, contained comparatively little volatile organics as defined by the protocol for Total Chromatographable Organics.

LC FRACTIONATION OF CONDENSABLE ORGANICS FROM KOSOVO STREAMS

The mass distribution of organic matter in the Kosovo condensates, as determined by the EPA Level 1 fractionation protocol, is shown in Table 6. All data are given as stream concentration, expressed in mg/m^3. In this form, the values shown for each fraction do not indicate the mass recovered from the column, but rather the computed mass concentration in one cubic meter of gas. Therefore, fraction concentrations are directly relatable to stream concentrations.

TABLE 6. CONCENTRATIONS OF ORGANICS FOUND IN EACH LIQUID CHROMATOGRAPHIC FRACTION AND IN THE SAMPLE STREAM

Source	LC Fraction (mg/m^3) 1	2	3	4	5	6	7	Total Recovered mg/m^3	Concentration* in Stream mg/m^3
Fleissner Autoclave Vent	229	47	80	47	73	203	20	699	1,114
LP Coal Lock Vent	167	79	426	1,456	1,281	2,297	266	5,981	7,739
HP Coal Lock Vent	395	285	145	168	282	563	67	1,912	2,872
Start-up Vent	458	430	1,743	160	268	1,595	302	4,956	5,540
H_2S-Rich Waste Gas	19	5	12	7	8	18	4	73	130
Tar Tank Vent	3,734	449	410	652	753	2,179	225	8,402	14,412
Medium Oil Tank Vent	2,275	229	246	250	335	1,061	76	4,471	21,118
Tar Separation Waste Gas	266	105	154	129	183	649	38	1,525	3,302
Phenolic Water Tank Vent	32,190	3,335	2,458	3,650	4,185	10,847	857	51,737	124,884
Ammonia Stripper Vent	1,880	2,607	2,222	16,923	17,692	27,949	4,145	73,419	99,218
Naphtha Storage Tank Vent	342	25	40	44	34	380	37	902	5,589

All values computed to stream concentration and expressed as milligram per normal cubic meter of gas

*From Table 2.

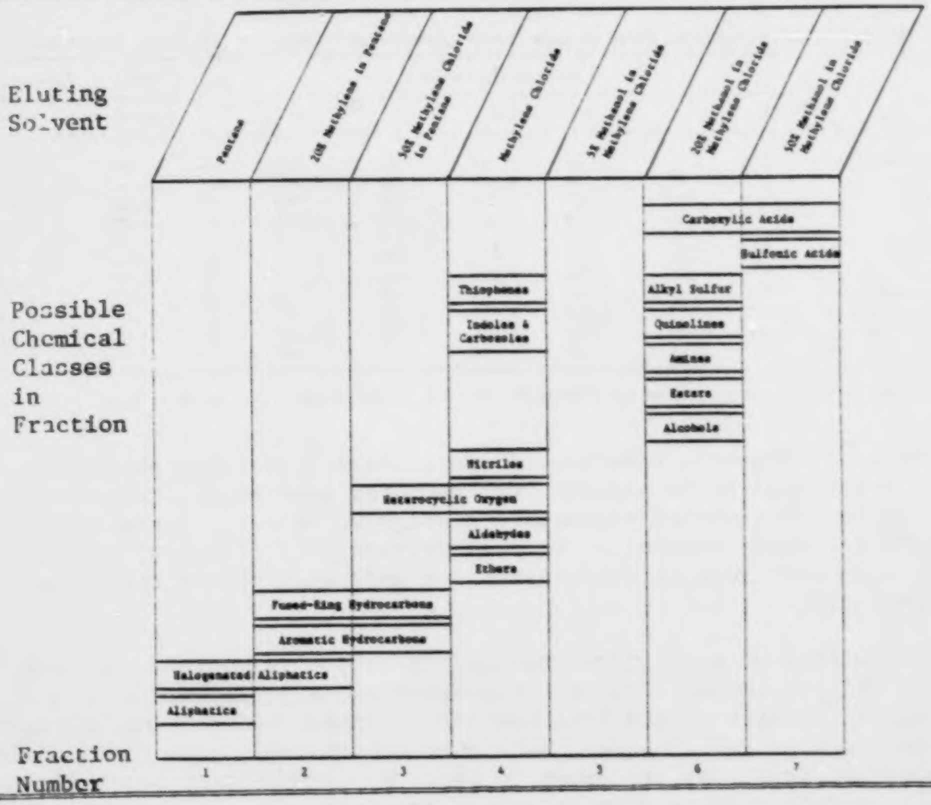
Recoveries of organics from the LC fractionation averaged about 50% (Table 7). Recoveries of VO and NVO were computed separately, consequently the values shown for combined organics are weighted values. These results show that NVO recovery, generally, was better than VO's recovery; probably because the component loss to evaporation was more significant than loss through non-elution.

The composition of each chromatographic fraction is defined, in part, by the polarity of the eluting solvent. Consequently, all components in a given chromatographic fraction should have similar polarity, but they may represent widely differing chemical classes. Some chemical classes which could be found in the respective fractions are shown in Table 8. Fraction 5, which shows no entry should contain overlap from adjacent fractions.

TABLE 7. RECOVERIES OF ORGANICS FROM THE LIQUID CHROMATOGRAPHIC PROCEDURE

Stream		Percent Recovery		
		Volatile Organics	Non-Volatile Organics	Combined Organics
Fleissner Autoclave Vent		41	70	62
LP Coal Lock Vent		109	47	77
HP Coal Lock Discharge		66	67	66
Gasifier Start-up Vent		45	54	49
H_2S-Rich Waste Gas		40	65	58
Tar Tank Vent		58	58	58
Medium Oil Tank Vent		17	93	21
Tar Separation Waste Gas		38	93	46
Phenolic Water Tank Vent		42	91	46
Ammonia Stripper Vent		98	43	74
Naphtha Storage Tank Vent		9	83	16
	Mean	43	69	53
	SD	±25	±18	±19

TABLE 8. PROBABLE LC FRACTION IN WHICH VARIOUS COMPONENT CLASSES APPEAR


Eluting Solvent
Pentane
20% Methylene in Pentane
50% Methylene Chloride in Pentane
Methylene Chloride
5% Methanol in Methylene Chloride
20% Methanol in Methylene Chloride
50% Methanol in Methylene Chloride
Possible Chemical Classes in Fraction
Carboxylic Acids
Sulfonic Acids
Thiophenes
Indoles & Carbazoles
Alkyl Sulfur
Quinolines
Amines
Esters
Alcohols
Nitriles
Heterocyclic Oxygen
Aldehydes
Ethers
Fused-Ring Hydrocarbons
Aromatic Hydrocarbons
Halogenated Aliphatics
Aliphatics
Fraction Number
1
2
3
4
5
6
7

The relative distributions of the eluted organics across the seven fractions are shown in Table 9. These results indicate that fraction 6, which should include phenols and nitrogen heterocyclics, contains the largest portion of the eluate (Ave = 31% ± 8) followed by fraction one [Ave = (27% ± 19)] which should contain only paraffins.

TABLE 9. PERCENT OF ELUTED ORGANICS FOUND IN EACH LC FRACTION AND PERCENT RECOVERY FROM THE LC SEPARATION PROCESS

Source	Total Elution mg/m³	Fraction Number							Percent Recovered
		1	2	3	4	5	6	7	
Fleissner Autoclave Vent	699	33	7	11	7	10	29	3	63
LP Coal Lock Vent	5,981	3	1	7	24	21	38	4	77
HP Coal Lock Vent	2,499	21	15	7	9	15	29	4	67
Start-up Vent	-	9	(9)	(35)	(3)	(5)	(32)	(6)	51
H_2S-Rich Waste Gas	59	25	7	17	10	11	24	6	56
Tar Tank Vent	8,402	44	5	5	8	9	26	3	58
Medium Oil Tank Vent	4,471	51	5	5	6	7	24	2	21
Tar Separation Waste Gas	1,525	17	7	10	8	12	43	3	46
Phenolic Water Tank Vent	57,522	56	6	4	6	7	19	2	46
Ammonia Stripper Vent	59,880	3	4	3	23	24	38	6	74
Naphtha Storage Tank Vent	902	38	3	4	5	4	42	4	16

A three-dimensional view of the relative distribution of chemical classes across the key streams in the Kosovo plant is shown in Figure 3. From this view, it is evident that a significant portion of the condensable organics from each stream is found in fraction 6 which contains phenols and nitrogen heterocyclics and that most streams contain relatively large proportions of alkyl aromatics as found in fraction 1. Fraction 3 is seen to be larger in the Start-Up Vent and H_2S-Rich Waste Gas's condensate. This fraction could contain thiophenes, indols, nitriles, and oxygen heterocyclics which are normally found in fraction 4 but probably overlap.

The low level of alkyl aromatics in the ammonia stripper vent condensate supports substantially the Phase II source test results which showed virtually no benzene or toluene in that vent's discharge.

A COMPARISON OF CONDENSABLE ORGANICS IN KOSOVO STREAMS WITH THOSE OF OTHER TYPES OF GASIFIERS

A comparison of the levels of condensable organics in vent gases from the Kosovo plant with those in *"similar"* streams from other types of gasifiers indicates that the organics concentration levels generally are comparable. The comparison data are shown in Table 10. The lower level of volatile organics in the Chapman coal vent discharge may be because the Chapman gasifier was using bituminus coal whereas all others listed were using lignite.

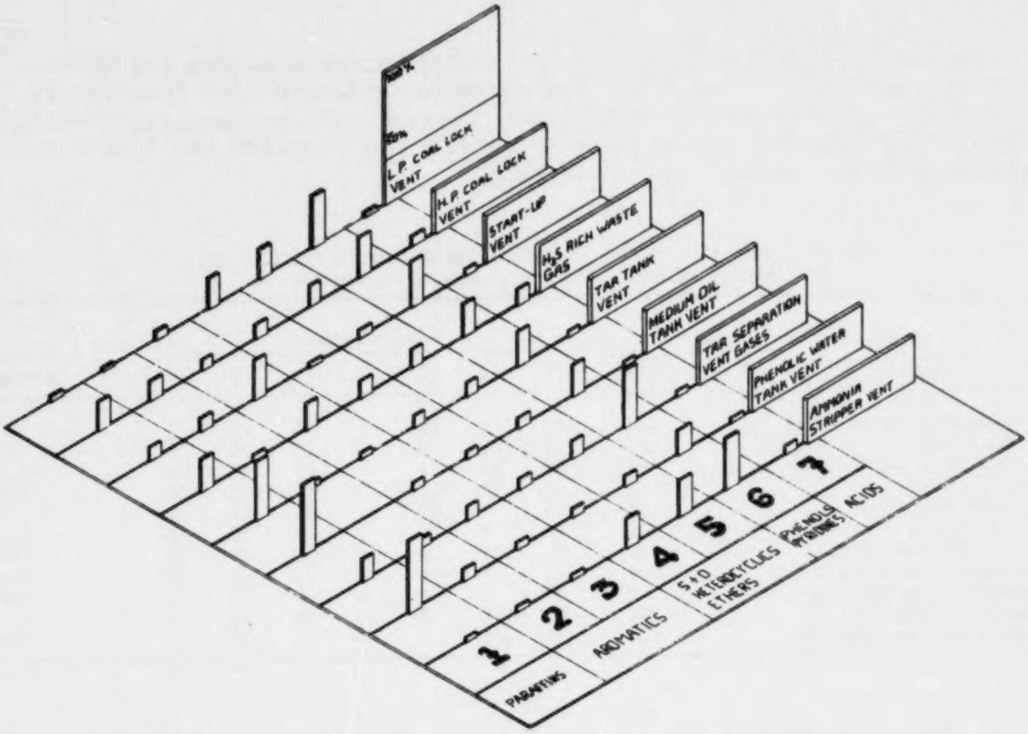


Figure 3. Distribution of Chemical Classes across the LC Fractions of Kosovo Gas Stream Condensates.

TABLE 10. A COMPARISON OF ORGANICS IN *"SIMILAR"* STREAMS FROM DIFFERENT GASIFICATION PLANTS (4-6)

	mg/m³		
Source	Volatile Organics	Non-Volatile Organics	Total Organics
Lurgi (Kosovo) LP Coal Lock	3,732	4,007	7,739
Lurgi (Kosovo) HP Coal Lock	2,121	1,632	3,753
Chapman (Holston) Coal Feeder Vent	378	2,002	2,380
Riley Product Gas	3,643	2,186	5,829
Wellman-Galusha (Ft. Snelling) Product Gas	5,900	2,100	8,000
Kosovo Tar Separation Offgas	2,335	967	3,302
Chapman Separator Vent	1,897	2,303	4,200

CHARACTERIZATION OF KOSOVO PROCESS LIQUIDS AND SOLID WASTES

The concentrations of organics in Kosovo process liquids and solid wastes are summarized in Table 11. These results indicate that phenolic water is transporting approximately 11 g/ℓ of organics of which 32% are volatile. Heavy tar consists of about 86% organics - the balance probably being a combination of error in the determination and inorganics in the coal; heavy tar is known to contain a considerable amount of coal dust (26% insoluble particles). Gasifier ash, also listed in Table 11, contains minimal organic matter (.04%) of which none was volatile.

TABLE 11. CONCENTRATIONS OF VOLATILE AND NON-VOLATILE AND TOTAL ORGANICS IN KOSOVO PROCESS LIQUIDS AND SOLID WASTES

	Units	Volatile Organics	Non-Volatile Organics	Total Organics	Percent Volatile	Percent Non-Volatile
Phenolic Water	mg/l	3,569	7,556	11,225	32	68
	mg/l	3,774	7,371	11,145	34	66
Medium Oil	mg/g	389	439	828	47	53
	mg/g	334	452	786	42	58
Tar	mg/g	567	778	1,345	42	58
Heavy Tar	mg/g	460	404	864	53	47
Gasifier Ash	mg/kg	-	400	400	0	100

For definition of volatile and non-volatile, see Table 2.

The by-products, tar and medium oil, show very similar distributions between volatile and non-volatile organics. When their vastly differing boiling point ranges are considered, this similarity is surprising. However, the low recovery of total organics from the medium oil suggests that a significant amount of sample was lost in the determination (∿20%). If a correction for this loss were applied to the volatile organics, a more reasonable value would be obtained (55%).

The distribution of organics in various Kosovo tars and oils as determined by liquid chromatography is shown in Table 12. Although these materials can be expected to have vastly different compositions, as would be indicated by their differing solubilities and boiling point ranges, they have surprisingly similar chromatographic profiles.

The close similarity in the LC profiles from the Kosovo streams, whose chemical compositions may differ significantly indicates that more discriminating methods of separation and detection are needed to obtain descriptive profiles of these streams.

GAS CHROMATOGRAPHIC ANALYSIS WITH ELEMENT SPECIFIC DETECTORS

As a supplement to the information that was provided by the LC Fractionation, the condensable organics from several streams were examined by gas

TABLE 12. PERCENT ELUTED ORGANICS FOUND IN EACH LC FRACTION FROM THE LC SEPARATION OF SEVERAL KOSOVO LIQUIDS AND HEAVY TAR

	Percent in Each Fraction			
Fraction	Phenolic Water	Heavy Tar	Tar	Medium Oil
1	19	10	17	12
2	15	6	2	6
3	19	16	15	16
4	4	11	9	4
5	10	14	9	10
6	31	39	39	45
7	2	4	9	7

chromatography with element specific detectors. Chromatograms of the sulfur-containing species and of the nitrogen-containing species that were obtained in this manner show that the Kosovo streams contained complex mixtures of both types of compounds.

The sulfur-specific chromatograms of condensable organics from three streams in Figure 4 show both similarities and differences in these materials. For example, the chromatograms of the LP and the HP coal lock vent have many peaks in common, while the chromatogram of the ammonia stripper condensate is distinctly different from those of the coal lock condensates. The stripper condensate may contain a relatively larger amount of the more water soluble sulfur-containing species.

The condensate from the HP coal lock shows considerably less background matrix effect which may relate in part to the influences of the Venturi scrubber through which the gas had passed. The peaks labeled 1-4 have been identified as thiophenes. Peaks labeled 5-8 are unidentified; however, their intensity suggests that they represent materials which contain a higher sulfur to carbon ratio than the thiophenes (possibly two or more sulfurs per molecule, e.g., disulfides or dithiols). Their uniform difference in retention suggests that they may be an homologous series of isomers.

Nitrogen-specific chromatograms of the stream condensates indicate that the Kosovo condensable organics contain several classes of organic nitrogen compounds. The chromatogram of the condensates from four streams, shown in Figure 5, indicate that these samples contained many of the same components. Several peaks have been identified tentatively as isomers of pyridine and quinoline. In contrast, the chromatograms in Figure 6 indicate that the nitrogen species in some streams differ significantly from the others. For example, the chromatogram of the condensable organics from the stripper vent (A) and the medium oil tank (C) differs significantly from that of the phenolic water tank vent (B). (The latter chromatogram (B) is similar to those in Figure 5). These results indicate that the major components in the two groups of samples are different compounds rather than the same compounds which have distributed differently between the two groups of streams.

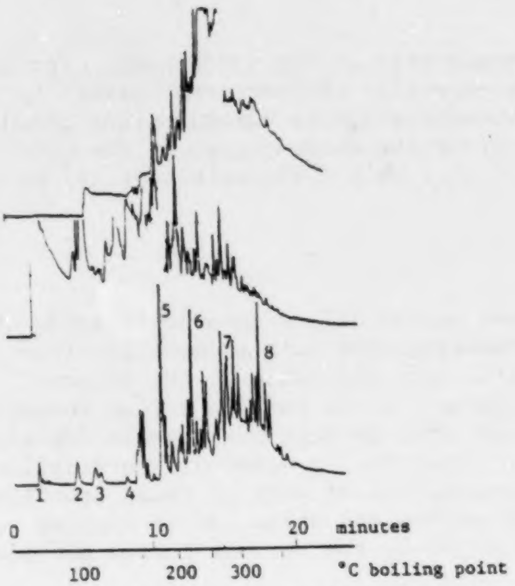


Figure 4. Chromatograms of Sulfur Species in Condensates from 3 Kosovo Gas Streams.

Top - LP Coal Lock
Center - Ammonia Stripper Vent
Bottom - HP Coal Lock

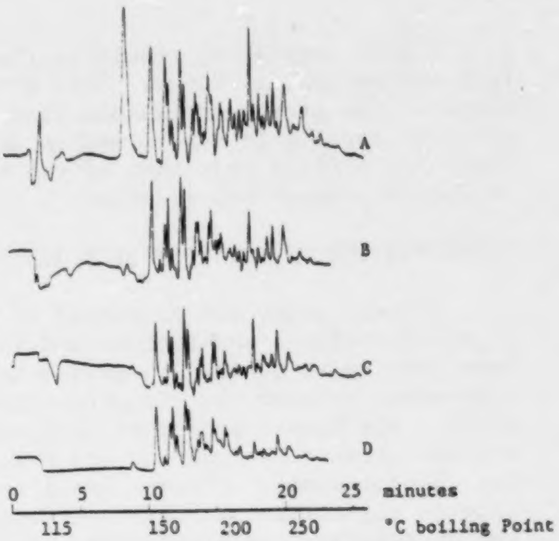


Figure 5. Chromatograms of Nitrogen Species in Condensates from 4 Kosovo Gas Streams.

A - LP Coal Lock Vent
B - HP Coal Lock Vent
C - Tar Separation Waste Gas
D - Tar Tank Vent

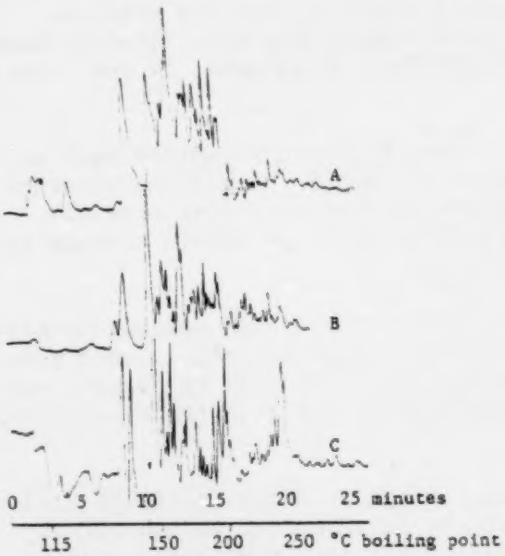


Figure 6. Chromatograms of Nitrogen Species in Condensates from 3 Kosovo Streams.

A - Ammonia Stripper Vent
B - Phenolic Water Tank Vent
C - Medium Oil Tank Vent

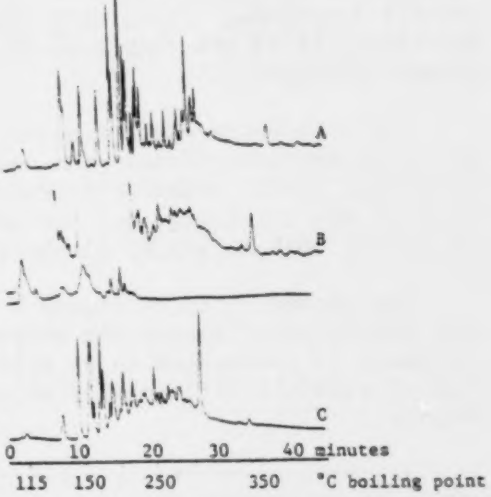


Figure 7. Chromatograms of Nitrogen Species in Kosovo Medium Oil.

A - Neutral Fraction
B - (2) Base Extractable Fraction (contains acids & phenols)
C - Acid Extractable Fraction (contains organic bases)

A most surprising result is the chromatogram of the condensable organics from the medium oil tanks. This nitrogen-specific chromatogram differs from those of the other streams and from previously prepared chromatograms of the nitrogen species in Kosovo medium oil. Since the chromatogram of the condensed discharge differs from that of the tank's oil, this condensate must not be a product of simple vaporization.

INVESTIGATION OF KOSOVO MEDIUM OIL

A brief study was conducted on Kosovo medium oil using a combination of physical/chemical separations and gas chromatography with element specific detectors in an attempt to gain some insite into the cause of the observed difference between the elemental chromatograms of the various stream condensates. The Kosovo medium oil was separated into an acid-extractable fraction, a base-extractable fraction and a neutral fraction. A water-oil co-distillate was also obtained. Element specific chromatograms of each of these fractions provide significant information about the medium oil which can be applied to the condensable organics which are transported by the various Kosovo gaseous streams.

The nitrogen-bearing species in Kosovo medium oil were found to be more complex than the sulfur species in that they consisted of a complex mixture of several different classes of compounds whose solubilities were markedly affected by pH. The chromatograms in Figure 7 show that three distinctly different sets of compounds are found in the respective neutral, base extractable and acid extractable fractions, and that each fraction contains numerous (40-60) compounds. Since very few peaks show common retention times between fractions, it is reasonable to conclude that there is minimal, if any, overlap between fractions.

The acid extractable fraction should contain proton acceptors such as pyridines and quinolines: the neutral fraction should contain the pyrazine (diazines) and/or other more neutral nitrogen species including possibly oxazoles and thiazoles; and the base extractable fraction should contain proton donors such as acids, alcohols and phenols.

The chromatogram in Figure 8 was obtained with the NaOH soluble material that precipitated during the acid-extraction of the medium oil. Since pyroles are known to polymerize in an acid medium and since the peak at 35 min. matches that of cabazole (dibenzopyrole) it is conceivable that this fraction contains pyroles.

A chromatogram of the water/oil co-distillate is shown in Figure 9 along with a chromatogram of the vapor over a closed container of medium oil at about 50°C. This comparison shows that except for the broad early eluting peaks in the vapor, the two samples contain many of the same compounds. The broad early eluting peaks in the vapor suggest that the vapors contain low boiling, strongly polar nitrogen species which are interacting with the column. These materials have not been identified or quantified in the Kosovo gas streams.

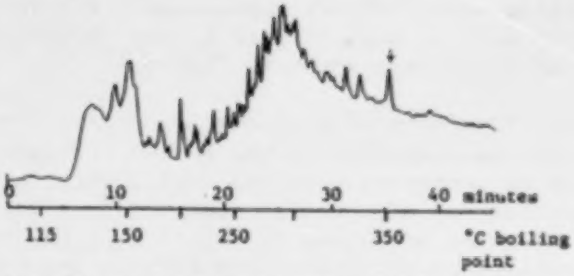


Figure 8. Chromatogram of Acid Insolible Fraction from Kosovo Medium Oil. Identified peak (↓) has same retention time as Carbazole.

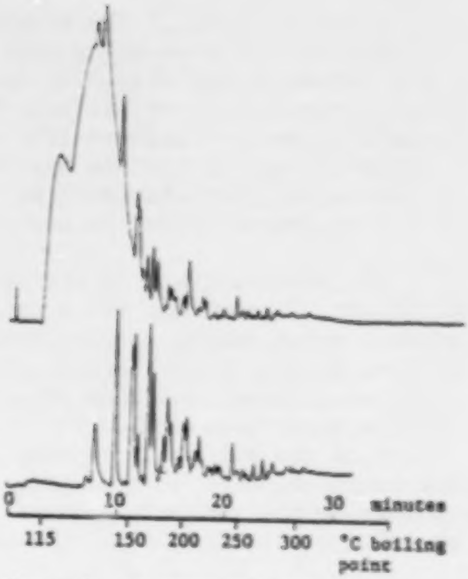


Figure 9. Chromatograms of Nitrogen Species in Medium Oil Head Space Vapor (top) and in Water-Oil Co-distillate (bottom).

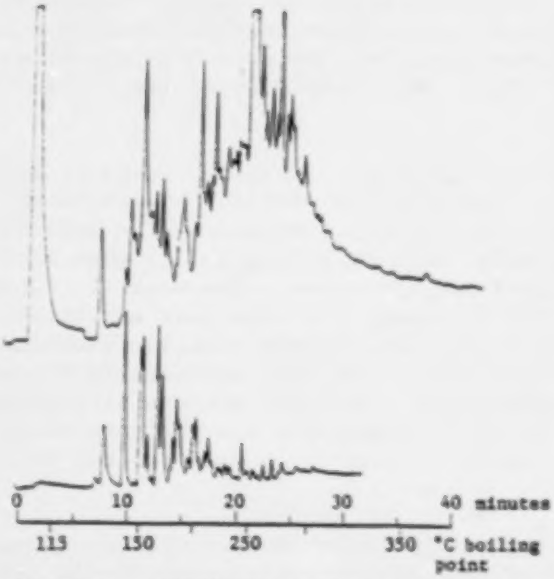


Figure 10. Chromatogram of Nitrogen Species in Residual Water from Co-distillation of Kosovo Medium Oil (top) Compared with Chromatogram of Nitrogen Species in Water-Oil Co-distillate (bottom).

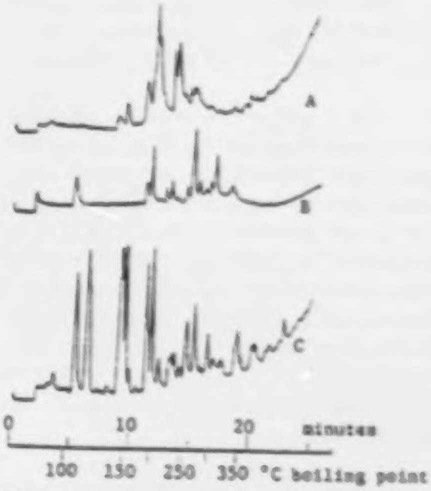


Figure 11. Chromatograms of Sulfur Species in Fractions of Kosovo Medium Oil.

A - Acid Extractable Fraction
B - Base Extractable Fraction
C - Neutral Fraction

A chromatogram of the residual water from the co-distillation (still pot) is shown in Figure 10 along with a chromatogram of the steam distillate. These chromatograms also have many peaks in common, but the two materials differ greatly in composition. Significant quantities of high molecular weight materials have partitioned into the water layer from the medium oil producing a fraction that is rich in high-boiling water soluble components. A portion of the water layer chromatogram (5-15 min) is very similar to the chromatogram of the condensate from the ammonia stripper vent shown in Figure 6.

The chromatograms of the several fractions of medium oil shown in Figures 6 through 10 show that the organic nitrogen species in the Kosovo organics represent an extremely complex mixture of compounds covering a wide range of boiling points, solubilities, polarities and dissociation potentials. However, when these compounds are fractionated according to solubility, pH, and finally vapor pressure, a set of profiles is obtained which defines the composition of the mixture. Because these fractionation methods are not absolute, the composition of each fraction depends upon the separation method used, as-well-as on the sample's compositions. Consequently, the influence of the separation method must be considered when interpreting results.

A major factor in the complexity of the mixture of nitrogen compounds is that the nitrogen species are influenced by so many different properties. The stream's composition can be altered significantly by a slight change in pH, or by the presence or absence of water or by an increased organic layer in an aqueous process stream. Further, a sample's composition can also be influenced by a vapor collection method as well as by a vapor recovery method. As was demonstrated here, exposing a sample to a strong acid can remove an entire class of components. Consequently, a characterization based on a well defined methodology, that takes into consideration the specific properties of these nitrogen compounds, is needed before the composition of the Kosovo organics can be defined quantitatively.

The sulfur species in Kosovo medium oil also represent a range of solubilities and dissociation potentials. However, the mixture appears to be somewhat less complex than the mixture of nitrogen compounds. The neutral fraction of medium oil contains many more components (Figure 11) than either the acid extractable or the base extractable fractions. The neutral fraction contains primarily the thiophenes and the mercaptans. The base extractable fraction which should contain organic acids, and phenols probably contains bifunctional (oxygen and sulfur) compounds also. The acid extractable fraction, which was shown to contain the nitrogen bases, must also contain bifunctional compounds such as thiozoles. Both the acid extractable and the base extractable sulfur compounds appear to fit into a comparatively well defined boiling point range.

When the sulfur specific chromatograms of Kosovo medium oil fractions are compared with those of the plant's discharge stream condensates, it is apparent that the neutral components are dominant in the gas streams associated with the product gas. In contrast, the chromatogram of the ammonia stripper vent shows numerous peaks which match the profiles of the acid and base extractable fractions of medium oil, supporting the earlier premise that the ammonia stripper condensate contains higher concentrations of the water soluble sulfur species. Bifunctional compounds such as thiozoles (S & N) and thiophenols (S & O), exhibit higher water solubilities than thiophenes and may well be present in the stripper vent's discharge.

POLYNUCLEAR AROMATICS (PNA'S) IN KOSOVO STREAM CONDENSATES

The concentrations of four hazardous polynuclear aromatics (PNA's) in several Kosovo discharge streams are shown in Table 13. Highest concentration levels were found in the LP coal lock discharge. The higher sensitivity levels achieved for the naphtha storage tanks were achieved by concentrating the sample enough to obtain a measurable level of PNA. The concentration of BAP in the naphtha storage tank was thereby measured at a level of 0.085 $\mu g/m^3$. For the remaining streams, PNA concentrations were measured to a sensitivity level of 0.1 ppm on the extracts as defined by the protocol shown in Figure 3. The resulting minimum detectable concentrations calculated for each stream are listed in Table 13.

TABLE 13. CONCENTRATIONS ($\mu g/m^3$) OF SELECTED HAZARDOUS POLYNUCLEAR AROMATICS IN KOSOVO GASEOUS DISCHARGE STREAMS

Source	BaA	BaP	dBahA	BhF
LP Coal Lock Vent	163	670	52	670
Ammonia Stripper Vent	85	20	<2.1	12
Naphtha Storage Tank Vent	<0.06	0.085	0.06	0.11
Start-up Vent	-	139	<2.1	-
Tar Tank Vent	-	252	<10	-
Phenolic Water Tank Vent	-	<50	<50	-
Medium Oil Tank Vent	-	<6.5	<6.5	-
H_2S-Rich Waste Gas	-	<0.6	<0.6	-
CO_2-Rich Waste Gas	-	<0.7	<0.7	-

All (<) values are calculated from a minimum detectable concentration of 0.1 ppm in the measuring solution.

- not determined.

BaH - Benzo(a)anthracene
BaP - Benzo(a)pyrene
dBahA - dibenz(ah)anthracene
BhF - Benzo(h)Fluoranthene

In a previous report (1) the concentration level of PNA in the Kosovo coal lock discharge was estimated from the concentration of PNA in by-product oil using the measured level of tars and oils in the discharge as a base for calculation. The level for BAP in the LP coal lock discharge was estimated to be between 500 $\mu g/m^3$ (the oil based value) and 1500 $\mu g/m^3$ (the tar based value). The measured value on the stream is 670 $\mu g/m^3$ which is very close to the estimate that was based on medium oil. This agreement indicates that the reasonable estimates of the levels of PNA in discharge streams can be made with the combined use of the concentration of tar/oil aerosols in the streams and the PNA concentration of medium oil.

Estimated values that were reported previously for 7,12 Dimethylbenz(a)-anthracene could not be confirmed because difficulty was experienced in the determination. Reproducible results could not be obtained.

ENVIRONMENTAL SIGNIFICANCE OF CONDENSABLE ORGANICS IN KOSOVO STREAMS

In a previous work, the environmental significance of each of these Kosovo streams was determined using the SAM-1/A model to compute the streams' Total Discharge Severities (TDS). To make these determinations, the concentrations of each potential pollutant in the gas phase was divided by its D-MEG value to obtain component DS values which could be summed to obtain the streams' TDS value (7).

To include the contributions of the condensable organics in the stream's TDS determination, it is necessary to adopt a representative D-MEG value with which to calculate Discharge Severity (DS) values for these heterogeneous mixtures of organic substances. Use of a representative D-MEG value is the only reasonable alternative since a rigorous treatment based on individual component concentrations and D-MEG values is impractical, if not impossible.

A D-MEG (air-health) value of 2.5×10^4 was adopted as being representative of higher molecular weight components thought to be present in the Kosovo organic condensates. This value was used to calculate DS values as shown in Table 14 for condensates in each stream. Also shown are: the previously reported TDS values that are based on the stream's major and minor components, and the percentages by which each stream's TDS would be increased by the addition of the DS due to condensable organics. No percentage value exceeded 20% and several were less than 1%.

TABLE 14. EFFECT OF CONDENSABLE ORGANICS ON TOTAL DISCHARGE SEVERITY (TDS) OF KOSOVO STREAMS

Source	Previously Reported TDS	Added DS*	% Increase
Fleissner Autoclave Vent	1.00E04	4.50E01	<1
LP Coal Lock Vent	7.88E03	3.10E02	4
HP Coal Lock Vent	5.92E03	1.15E02	2
Start-Up Vent	7.19E03	3.89E02	5
H_2S-Rich Waste Gas	1.11E04	5.20E00	<1
CO_2-Rich Waste Gas	7.32E02	5.60E01	<1
Tar Tank Vent	4.31E03	5.76E02	13
Medium Oil Tank Vent	2.82E04	8.44E02	3
Tar Separation Waste Gas	2.06E04	1.32E02	6
Phenolic Water Tank Vent	3.67E04	5.00E03	14
Ammonia Stripper Vent	2.07E04	3.97E03	19
Naphtha Storage Tank Vent	7.08E04	3.23E02	<1

*Based on an average D-MEG (air-health) of 2.5E04
1.00E04 represents 1.00×10^4

These results indicate that the "condensable" organics are environmentally significant in all streams except the CO_2-Rich Waste Gas but, in all cases, their contributions to the TDS values of these streams are relatively small.

ENVIRONMENTAL SIGNIFICANCE OF HAZARDOUS PNA'S IN KOSOVO STREAMS

DS (air-health) values for the potentially more significant PNA's are listed in Table 15 along with the percentages by which these DS's would increase the previously reported TDS values of each stream. As with the condensable organics, all DS values greater than unity are potentially significant environmentally. However, significant increases in stream TDS value were found in only three of the nine streams tested. The greatest increase (430%) was seen in the LP coal lock vent; followed by the tar tank vent (300%) and the start-up vent (100%). A most significant observation is that the PNA's contribution to stream TDS is dominated by the contribution from Benzo(a)pyrene.

TABLE 15. DISCHARGE SEVERITY DUE TO HAZARDOUS PNA'S IN KOSOVO STREAMS

Source	BaA	BaP	dBahA	Total	%
LP Coal Lock Vent	3.62E00	3.35E04	5.59E02	3.41E04	433
Ammonia Stripper Vent	1.89E00	1.00E03	2.26E01	1.02E03	5
Naphtha Storage Tank Vent	-	4.25E00	<1	4.25E00	nil
Start-Up Vent	-	6.95E03	<2E1	6.97E03	97
Tar Tank Vent	-	1.26E04	<1E2	1.27E04	297
Phenolic Water Tank Vent	-	<2E3	<5E2	<2.5E3	<7
Medium Oil Tank Vent	-	<3E2	<7E1	<3.7E2	<1
H_2S-Rich Waste Gas	-	<3E1	<6E0	<3.6E1	<1
CO_2-Rich Waste Gas	-	<4E1	<8E0	<4.8E1	<7

All DS values for Benzo(h)fluoranthene were <1 and are not shown.

ACKNOWLEDGEMENT

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PB83-128207

APPLICATION OF KOSOVO (LURGI) GASIFICATION † PLANT TEST RESULTS TO POLLUTION CONTROL PROCESS DESIGN

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ABSTRACT

This paper describes a test program performed by Radian Corporation to obtain process data to define the pollution control technology requirements for Lurgi-based coal gasification plants. This program was sponsored by the Industrial Environmental Research Laboratory (IERL) of the U.S. Environmental Protection Agency conducted at a Lurgi-based gasification plant in the Kosovo region of Yugoslavia. It should be emphasized that the Kosovo plant does not reflect state-of-the-art Lurgi technology especially in pollution control practices. However, the "uncontrolled" process discharge streams from the Kosovo plant are representative of those from Lurgi-based gasification plants.

From an assessment of the Kosovo data, the following discharge streams were selected to be "key" based on flow rate and/or concentration of pollutants (1) high- and low-pressure coal lock vent gases and ash from the gas production section, (2) liquid depressurization gases and surge tank vent gases from the tar/oil separation section, (3) H_2S- and CO_2-rich vent gases from the Rectisol acid gas removal section, and (4) extracted wastewater from the Phenosolvan unit.

The conclusions reached from an engineering evaluation of the components in those key discharge streams and the effects those components may have on pollution control processes were as follows: (1) pollution control processes are commercially available for treating these streams, (2) the effects of minor and trace components on the performance of those control processes have not been demonstrated and there may be problems in the direct transfer of technology from other industries (e.g., coke ovens), (3) the design and selection of pollution control processes during transient and normal operation should occur in parallel with the base plant design, and (4) the variability of the components in the discharge streams must be determined and included in pollution control process design.

INTRODUCTION

An international program, sponsored by the Industrial Environmental Research Laboratory (IERL) of the U.S. Environmental Protection Agency, was conducted in the Kosovo region of Yugoslavia. The major objective of this program was to characterize process discharge streams associated with a Lurgi-based gasification plant and to assess how components in those streams may affect pollution control process design and operation. The study, conducted over a three year period, was a cooperative endeavor between scientists from Yugoslavia, the EPA, and Radian. The program was undertaken because the Lurgi gasification process has significant potential for use in the United States.

The purpose of this paper is to address the key process discharge streams from the Kosovo plant that will require pollution control in a Lurgi-based plant constructed in the United States. The potential impacts of specific components in those key uncontrolled discharge streams on the design and operation of pollution control process are examined.

It should be emphasized that the Kosovo plant does not reflect state-of-the-art Lurgi technology and that it has essentially no pollution control processes that would be acceptable for Lurgi-based plants built in the U.S. However, the "uncontrolled" process discharge streams from the Kosovo plant contain compounds that will be present in discharge streams from U.S. Lurgi plants. Many of these species will affect the design and operation of pollution control processes in the first generation Lurgi-based gasification plants.

DESCRIPTION OF THE KOSOVO GASIFICATION FACILITY

The Kosovo gasification plant is an integral part of a large mine-mouth industrial complex located near the city of Pristina in the Kosovo Region of Southern Yugoslavia. The industrial complex consists of a coal mine, a coal preparation plant, the gasification plant, an ammonia plant, an air separation plant, and a steam and power generation plant. The gasification plant consumes dried lignite and produces two primary products: a fuel gas with a net heating value of 14 MJ/m^3 @ 25°C (360 Btu/scf) and hydrogen for ammonia synthesis. Several hydrocarbon by-products are also produced and are used as fuel. These by-products include: light tar, medium oil, naphtha, and crude phenols.

The design flow rates for the major streams in the Kosovo plant are shown in Figure 1. These flow rates are for five of the six Lurgi gasifiers in operation. As shown in Figure 1, the plant is designed to produce 24 Mg (65,000 m^3 @ 25°C) of product gas for 80 Mg of dried lignite consumed.

The unit operations employed at the Kosovo gasification plant are typical of the operations in several proposed U.S. Lurgi-based plants. Figure 2 is a simplified flow diagram of the unit operations in the Kosovo facility.

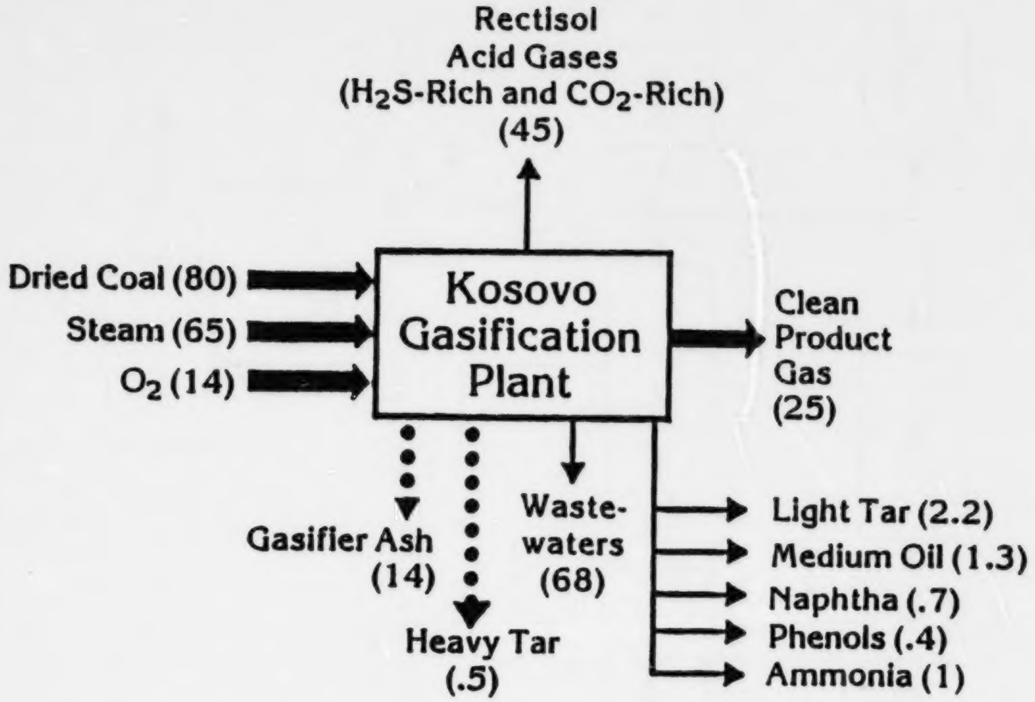
Rectisol
Acid Gases
(H2S-Rich and CO2-Rich)
(45)
Dried Coal (80)
Steam (65)
O2 (14)
Kosovo Gasification Plant
Clean Product Gas (25)
Gasifier Ash (14)
Heavy Tar (.5)
Wastewaters (68)
Light Tar (2.2)
Medium Oil (1.3)
Naphtha (.7)
Phenols (.4)
Ammonia (1)

Figure 1. Design Flow Rates of Major Streams for the Kosovo (Lurgi) Gasification Plant (Flow Rates in Megagrams/hr.)

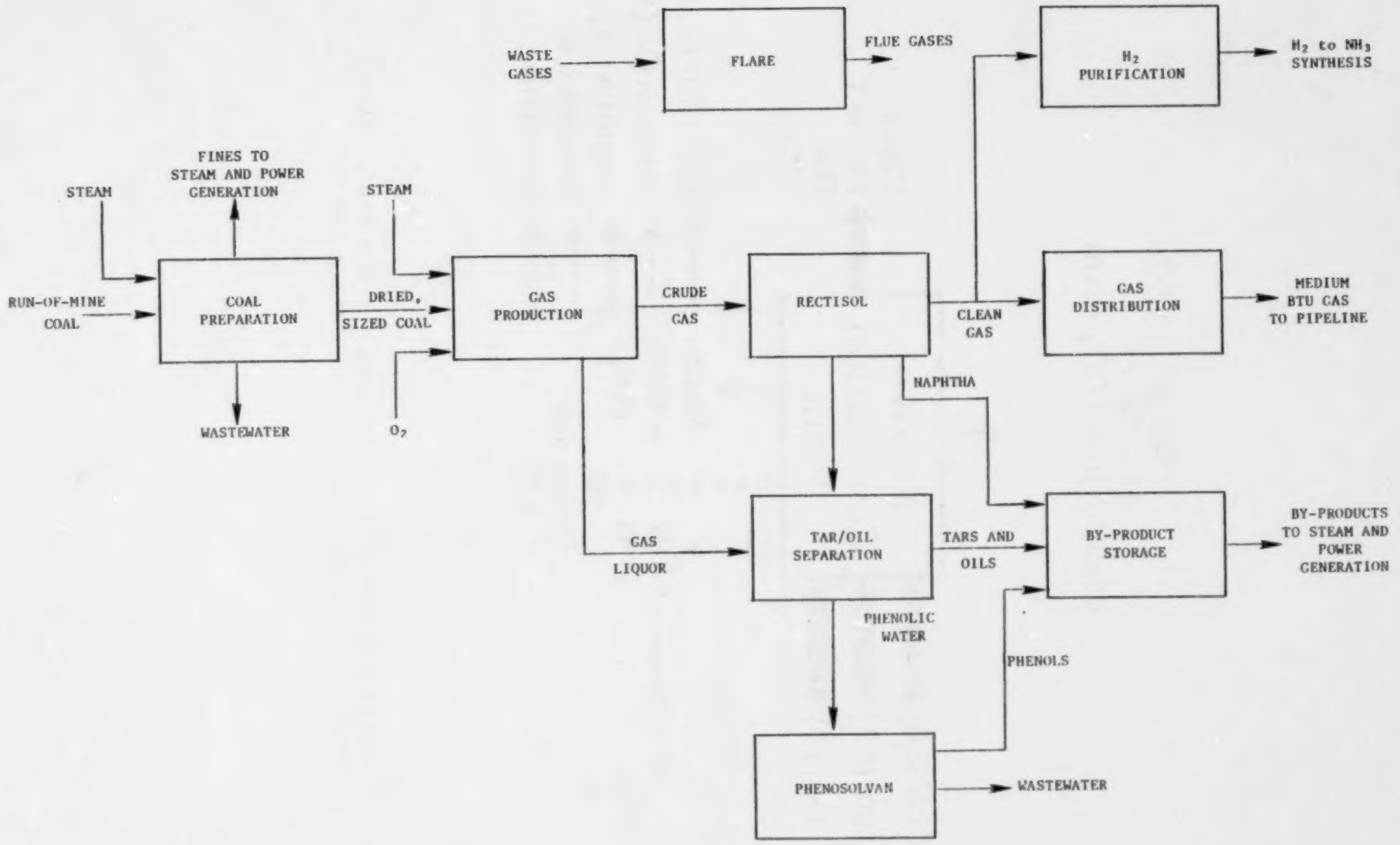
WASTE GASES
FLARE
FLUE GASES
H_2 PURIFICATION
H_2 to NH_3 SYNTHESIS
FINES TO STEAM AND POWER GENERATION
STEAM
RUN-OF-MINE COAL
COAL PREPARATION
WASTEWATER
STEAM
DRIED, SIZED COAL
O_2
GAS PRODUCTION
CRUDE GAS
RECTISOL
CLEAN GAS
GAS DISTRIBUTION
MEDIUM BTU GAS TO PIPELINE
NAPHTHA
GAS LIQUOR
TAR/OIL SEPARATION
TARS AND OILS
BY-PRODUCT STORAGE
BY-PRODUCTS TO STEAM AND POWER GENERATION
PHENOLIC WATER
PHENOLS
PHENOSOLVAN
WASTEWATER

Figure 2. Simplified Flow Diagram of the Kosovo Coal Gasification Plant

The following summarizes the function of each unit operation, its discharge streams, and those discharge streams considered to be key. Key discharge streams were selected based on two criteria: mass flow rate and/or high concentrations of pollutants.

COAL PREPARATION

Run-of-mine coal containing approximately 50 weight percent moisture is dried by the Fleissner process to approximately 25 weight percent moisture. The dried coal is then crushed and particles between 6 and 60 mm are stored in the gasifier coal feed hopper. Table 1 shows a typical composition of the dried coal feedstock. Coal fines (less than 6 mm) are routed to the on-site steam and power plant.

Although the Fleissner process is used in foreign countries, the process is not likely to be used in U.S. Lurgi plants. Therefore, the discharge streams from this process were not considered "key" with respect to the evaluation of pollution control requirements for U.S. facilities.

GAS PRODUCTION

In the gas production section, dried coal is reacted with steam and oxygen at a pressure of 25 atm to produce a crude product gas. This reaction occurs in the gasifiers (3.5m in diameter) used at Kosovo. The crude product gas is then cooled and scrubbed to remove coal fines, tars, oils, and other condensibles. Ash produced during gasification is collected from the bottom of each gasifier in a lock hopper. The ash is water-quenched and routed to a landfill.

The discharge streams from the gas production section are: coal room vent, high-pressure coal lock vent, low-pressure coal lock vent, start-up vent, gas liquor tank vent, ash lock vent, gasifier ash, and ash quench water. Of these discharge streams, the following are considered to be key streams:

- low-pressure coal lock vent,
- high-pressure coal lock vent, and
- gasifier ash.

TAR/OIL SEPARATION

In the tar/oil separation section, heavy tar, light tar, and medium oil are separated from the crude gas quench liquor and from the condensates produced by cooling the crude gas. Depressurization of quench liquor and condensates followed by a series of phase separators are used to accomplish this. Light tar and medium oil are sent to by-product storage to be used as boiler fuel. Heavy tar is landfilled at Kosovo; however, current plans for U.S. plants are to recycle this tar to the gasifier or to use it as boiler fuel. The aqueous phase from the separators is routed to Phenosolvan for phenol recovery.

TABLE 1. TYPICAL COMPOSITION OF THE DRIED COAL FEEDSTOCK FOR THE KOSOVO PLANT

Ultimate Analysis (wt. %)	
Moisture	20
Ash	14
Carbon	45
Sulfur	0.89
Hydrogen	3.5
Nitrogen	1.1
Oxygen	16
Heating Values (kcal/kg)	
Proximate HHV	3900
Proximate LHV	3700

The discharge streams from this unit operation are: depressurization gases, surge tank vents, phenolic water, and heavy tar. The key discharge streams include depressurization gases and surge tank vents.

ACID GAS REMOVAL (RECTISOL)

Acid gases, such as H_2S, COS, CO_2, HCN, and mercaptans are selectively removed from the cooled product gas by sorption in cold methanol. The product gas enters the Rectisol process at about 22°C and 23 atm. The gas is cooled by a cold water wash followed by a cold methanol wash. Condensates from this initial cooling are a light organic phase (naphtha) and aqueous phase. Naphtha is sent to by-product storage to be used as fuel while the aqueous phase is routed to tar/oil separation. After the initial gas cooling step, the gas is scrubbed with cold methanol in the H_2S absorber. The H_2S-lean product gas is then sent to CO_2 absorption for final purification. During methanol regeneration, the acid gases removed from the product gas stream are stripped from the methanol which results in two waste gas streams H_2S- and CO_2-rich vent gases.

Discharge streams from the acid gas removal unit operation are:

- o H_2S-rich vent,
- o CO_2-rich vent,
- o naphtha, and
- o aqueous condensate.

Of these streams, the H_2S- and CO_2-rich vent gases are considered key.

PHENOL REMOVAL (PHENOSOLVAN)

In the phenol removal section, phenolic water from the tar/oil separation section is extracted with diisopropylether (DIPE) to remove phenolic compounds. To accomplish this, residual tars and oils are removed by phase separation and filtration, followed by removal of dissolved gases by steam stripping. After dissolved gas removal, the water is extracted with DIPE to remove phenolic compounds. Recovered phenol is sent to by-product storage to be used as a fuel. The extracted water is discharged.

The discharge streams from the Phenosolvan section include:

- o stripped gases,
- o surge tank vents,
- o by-product phenol, and
- o wastewater.

The key discharge stream from this unit operation is wastewater from DIPE extraction.

KEY DISCHARGE STREAMS

As discussed above the key discharge streams from the Kosovo plant that are of primary concern for proposed Lurgi-based plants in the U.S. are:

- Gas production
  - High-pressure coal lock vent
  - Low-pressure coal lock vent
  - Gasifier ash

- Tar/Oil Separation
  - Depressurization gases
  - Surge tank vents

- Acid Gas Removal (Rectisol)
  - H_2S-rich vent gas
  - CO_2-rich vent gas

- Phenol Recovery (Phenosolvan)
  - Extracted wastewater

These streams were selected as key discharge streams based on their flow rates and/or their concentration of pollutants. Tables 2 and 3 summarize the flow rates and compositions of these streams. The data in these tables are a portion of the results from the environmental test program performed at the Kosovo plant.

The following text contains a discussion of these key discharge streams which emphasize the components in each stream that will affect the design and operation of processes used for pollution control in U.S. Lurgi-based plants. The use of the hydrocarbon by-products as fuel and/or as feedstocks for petrochemical manufacturing is also addressed.

GAS PRODUCTION

High-Pressure Coal Lock Vent

The flow rate of the high-pressure coal lock vent stream is approximately 2 percent of the crude product gas flow rate. This stream will contain all of the compounds found in the crude product gas exiting the gasifier including coal fines, tars, oils, reduced sulfur compounds, HCN, NH_3, CO, H_2, etc.

Because of the high flow rate and energy content of this stream, viable control alternatives include recycle to the product gas or use as a fuel. For recycle to the product gas, entrained particulate matter and tar/oil aerosols need to be removed prior to compression to product gas pressure. Particulate and aerosol removal also will be necessary prior to combustion to minimize equipment fouling and buildup of tar in the gas lines. Flue gas control of gases resulting from the combustion of the high-pressure vent stream also will be necessary because of the high levels of sulfur compounds in this stream.

Low-pressure Coal Lock Vent

The flow rate of the low-pressure coal lock vent gas is low (less than 0.2 percent of the crude product gas flow), however this gas will contain

TABLE 2. KEY GASEOUS DISCHARGE STREAM COMPOSITIONS

Stream Parameter	Low-Pressure Coal Lock Vent	High-Pressure Coal Lock Vent (after scrubbing)	Tar/Oil Separation Depressurization Gases (after scrubbing)	Medium Oil Surge Tank Vent	H_2S-Rich Tail Gas	CO_2-Rich Tail Gas
Dry Gas Flow Rate (m^3/gasifier-hr @25°C)	21**	230**	28**	1.7**	3600***	3600***
Moisture Content (wt %)	44	11	7.7	8.4	3.9	5.1
Dry Gas Molecular Weight	23.5	24.9	39.0	32.5	43.0	42.2
Dry Gas Composition						
Fixed Gases (Vol %)						
H_2	37	32	21	<0.01	0.11	<0.01
O_2	0.27	0.24	<0.01	0.45	<0.01	<0.01
N_2	0.18	0.14	<0.01	1.1	<0.01	<0.01
CH_4	8.6	10.5	3.5	7.6	4.3	1.2
CO	14.6	12	1.1	5.9	1.1	<0.01
CO_2	36.5	42	77.5	56	88	94
Sulfur Species (ppmv)						
H_2S	13,000	3300	9000	20,000	43,400	39
COS	110	120	120	98	420	62
Methyl Mercaptan	420	480	2500	5200	2100	8.5
Ethyl Mercaptan	220	210	1600	2100	780	6.6
Hydrocarbons (vol %)						
C_2H_6	0.22	0.42	0.33	0.36	0.82	1.60
C_2H_4	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
C_3's	0.14	0.25	0.41	0.30	0.63	0.28
C_4's	0.05	0.11	0.41	0.23	0.32	<0.01
C_5's	<0.01	0.01	0.09	0.09	0.04	<0.01
C_6^{+}'s	0.12	0.08	1.3	2.4	0.21	NF
Light Aromatics (ppmv)						
Benzene	760	550	9800	7650	120	1.0
Toluene	220	100	1200	1800	8	< 1
Xylene, Ethylbenzene	75	38	150	140	NF	< 1
Phenols	5.7	2.5	4.2	110	< 1	NF
Higher Aromatics	NF	NF	4.9	NF	NF	NF
Nitrogen Species (ppmv)						
NH_3	2400	NF	19,300	19	2200	4.6
HCN	600	170	64	57	200	13
Particulate Matter (mg/m^3 @ 25°C)						
Total Particulates	8100	960	920	NS	NS	NS
Organics Contained in Particulate Matter*	7300	660	660	NS	NS	NS

*Organics include tars and oils which contain significant amounts of polynuclear aromatics as found in the Kosovo tar and medium oil by-products.

**Measured flow rates

***Design flow rates

NF: Not found

NS: Sample not obtained during the test program

TABLE 3. KEY LIQUID AND SOLID DISCHARGE STREAM COMPOSITIONS

Key Liquid Stream	
Stream Parameter	Extracted Wastewater from Phenosolvan
Design Flow Rate (m^3/gasifier-hr)	13
pH	9.6
Solids Analysis (mg/L)	
Total Solids	1,350
Suspended Solids	1,160
Dissolved Solids	190
Water Quality Parameters	
COD (as mg O_2/L)	7,910
Permanganate (mg/L)	4,040
BOD_5 (as mg O_2/L)	2,350
Aqueous Composition Data (mg/L)	
TOC	1,470
Total Phenols	230
Volatile Phenols	130
Free Ammonia	Tr
Fixed Ammonia	205
Cyanide	0.019
Nitrites	Tr
Nitrates	11.4
Pyridines	--
Chlorides	60
Fluorides	Tr
Total Sulfur	84
Sulfites	-
Sulfates	110
Sulfides	-
Thiocyanates	<75
Thiosulfates	Tr
PNA Analysis (mg/L)	
Benz(a)anthracene	NF
7,12-dimethylbenz(a)anthracene	NF
Benzo(a)fluoranthrene	NF
Benzo(a)pyrene	NF
3-methylcholanthrene	NF
Dibenz(a,h)anthracene	NF
252 Group (as BaP)	0.19

Key Solid Stream	
Stream Parameter	Gasifier Ash before Quenching
Design Flow Rate (Mg/gasifier-hr)	2.8
Ultimate Analysis (wt %)	
Moisture	2.1
Ash	94
Volatile	-
Fixed Carbon	1.7
Carbon Dioxide	-
Total Sulfur	0.15
Free Sulfur	-
Fixed Sulfur	-
Hydrogen	0.25
Nitrogen	0.03
Oxygen (By Difference)	2.3
Chlorine	0.04
Proximate Analysis (wt %)	
Moisture	2.1
Ash	94
Volatiles	6.5
Fixed Carbon	-
Total Sulfur	0.15
Trace Elements (mg/kg) by AA	
As	75
Be	2.5
Cd	69
Co	17
Cr	180
Cu	40
Hg	0.30
Mo	8.9
Ni	320
Pb	52
Sb	NF
Se	24
Sr	370
Tl	NF
V	100
Zn	2.1

Tr = Trace
NF = Not Found
- = Not Analyzed
AA: Atomic Adsorption Spectroscopy

pollutants found in the crude product gas (e.g., tars, oils, reduced sulfur compounds, HCN, CO, etc.). Even if these gases are diluted with air, they still will contain significant levels of tar/oil aerosols and reduced sulfur species and, therefore, should not be directly vented to the atmosphere.

A viable control of the low-pressure coal lock stream involves first minimizing its flow rate by controlling the pressure at which the low-pressure lock vent is opened (approximately 2 atm) followed by particulate and aerosol collection and then combustion (flaring). The major concern in controlling this stream is the pressure drop required to remove particulates and aerosols. To attain the required pressure for this, a blower may have to be installed in the vent line. If a blower is required, an explosive gas mixture may result due to the influx of air. Precautions must be taken to eliminate exposing the gas mixture to ignition sources.

Gasifier Ash

The gasifier ash is a key waste stream because of its high flow rate and the potential for the leaching of trace elements contained in the ash. However, leaching tests (RCRA and ASTM, Ref. 1 and 2) performed on the unquenched gasifier ash from Kosovo and on ashes from other gasifier processes show that the concentration of trace metals in the leachates are well below RCRA limits for hazardous wastes. Table 4 shows the results of the RCRA and the ASTM leaching tests on the gasifier ash from the Kosovo plant. As shown in this table, the trace element concentration in the leachates was between 10 and 1000 times lower than the RCRA limits for hazardous wastes.

There are two disposal aternatives for gasifier ash resource recovery or disposal in a nonhazardous waste landfill. It should be emphasized that the leaching tests were conducted on unquenched ash and the leaching properties of the ash could be significantly different if untreated process wastewaters were used to quench the ash. If process water is used for ash quench, the water should be treated to remove any toxic organics or trace elements that may render the ash to be classified as hazardous under RCRA.

TAR/OIL SEPARATION

Liquid Depressurization Gases and Surge Tank Vents

The combined flow rate of depressurization gases and surge tank vents is less than one percent of the crude product gas flow rate. However, these streams contain high levels of pollutants (e.g., H_2S, COS, mercaptans, HCN, and nonmethane hydrocarbons) which must be controlled.

Two viable control alternatives for these gaseous streams are.

- containment and collection followed by combustion with flue gas controls and
- containment and collection followed by the sulfur recovery process used to treat the H_2S-rich gas from Rectisol.

TABLE 4. GASIFIER ASH TRACE ELEMENT LEACHING RESULTS

	Leachate Concentration/RCRA Limits	
Element	RCRA Leachate	Neutral Leachate
As	0.001	0.002
Ba	0.03	0.001
Cd	<0.001	<0.004
Cr	0.06	0.10
Pb	0.002	0.01
Hg	<0.005	<0.020
Se	0.01	0.007
Ag	<0.0002	<0.0008

Use of the first control alternative may be complicated by the pressure differences of the gas streams and the physical location of vents in the plant. Routing these gases to sulfur recovery also may cause operational problems in the sulfur recovery process due to the presence of reduced sulfur compounds (COS, mercaptans), HCN, and hydrocarbons. These potential problems are discussed in the control alternatives for the H_2S-rich vent gas from Rectisol.

ACID GAS REMOVAL (RECTISOL)

H_2S-Rich Vent Gas

The H_2S-rich vent gas from the Rectisol acid gas removal process has a high flow rate (approximately 30 percent of the clean product gas flow rate) and contains pollutants. Table 5 summarizes the compounds of concern in this stream. As shown in this table, the H_2S-rich gas contains significant levels of H_2S, mercaptans, COS, HCN, and nonmethane hydrocarbons.

Of the many viable methods to control this stream, two methods were selected for discussion in this paper:

- H_2S concentration (e.g., routing the gas to an amine-based acid gas removal process to concentrate the H_2S to approximately 10 to 15 volume percent in the gas) followed by sulfur recovery using a Claus with a Claus tail gas cleanup process, or

- H_2S removal using a Stretford process followed by tail gas combustion.

If the first control alternative is used, problems may be caused be the production of organic sulfur compounds in the Claus process because of the high levels of hydrocarbons in the gas (ref. 3). Also, the effectiveness of the Claus and the Claus tail gas treatment processes in removing high levels of reduced sulfur and nitrogen compounds has not been demonstrated.

The Stretford process will not remove COS from the stream and HCN in the stream will cause formation of nonregenerable compounds in the Stretford solution (ref. 4). The fate of mercaptans in the Stretford process is uncertain (e.g., the removal of mercaptans by the Stretford solution and how mercaptans distribute between the Stretford tail gas and the oxidizer vent gas). Another concern with the Stretford process is the effect of contaminants in the gas on the purity of the by-product sulfur (e.g., organics in the gas may end up in the by-product sulfur) thus reducing the marketability of the sulfur.

CO_2-Rich Vent Gas

The CO_2-rich vent gas from the Rectisol process is a high volume stream (approximately 30 percent of the clean product gas flow) and contains pollutants as shown in Table 6. In certain designs of Lurgi-based plants, the CO_2-rich vent stream is vented directly to the atmosphere. However,

TABLE 5. POLLUTANTS IN THE H_2S-RICH GAS FROM RECTISOL TO BE CONTROLLED

Component	Concentration
Major (vol. %)	
H_2S	2-5
CH_4	4
Nonmethane Hydrocarbons	2
CO	1
Minor (ppmv)	
COS	400
Mercaptans	3,000
NH_3	2,000
HCN	200

TABLE 6. POLLUTANTS IN THE CO_2-RICH GAS FROM RECTISOL TO BE CONTROLLED

Component	Concentration
Major (vol. %)	
Nonmethane Hydrocarbons	2
Minor (ppmv)	
COS	50
Mercaptans	10
NH_3	5
HCN	10
H_2S	40

based on the results obtained at Kosovo, the amount of nonmethane hydrocarbons and mercaptans in the CO_2-rich stream may not allow direct discharge of this stream.

Venting of the CO_2-rich tail gas directly to the atmosphere would involve operating the Rectisol process such that the levels of nonmethane hydrocarbons and reduced sulfur compounds are significantly lower than levels found at Kosovo. If this cannot be accomplished, a nonselective Rectisol process configuration may be used which has only one vent gas containing components in both the H_2S- and CO_2-rich vent gases. Viable control alternatives for this stream would be similar to those for the H_2S-rich vent gas.

PHENOL RECOVERY (PHENOSOLVAN)

Extracted Wastewater

The extracted wastewater from the Phenosolvan process has a flow rate of approximately 0.8 kg of wastewater per kg of coal fed to the gasifier and contains significant levels of pollutants. These compounds include phenols, organic acids, refractory organics, cyanides, and ammonia.

A viable control alternative for this wastewater is removal of organics by biological oxidation followed by trace organic removal by carbon adsorption and possibly incineration. Biological oxidation and carbon adsorption will be effective in removing the major portion of the organics; however, removal of high molecular weight "refractory" organics by these processes has not been demonstrated.

Direct transfer of biological oxidation and carbon adsorption technologies from other industries (e.g., coke ovens) may not be entirely applicable. This is illustrated by comparing the organic fractions in wastewaters from the Kosovo plant, the Chapman low-Btu gasification plant, and a coke oven plant. Figure 3 shows the relative amounts of total organic carbon (TOC) remaining in these wastewaters after extraction with DIPE to simulate the phenosolvan process and after analytical extraction with methylene chloride. Both of the gasification wastewaters contain significantly higher amounts of nonextractable (refractory) organics than the coke oven wastewater. These organics are very polar and/or ionic in nature since extraction (including pH adjustment) would not remove them.

Some preliminary data on carbon adsorption of wastewaters from the Chapman low-Btu gasification plant indicate that carbon adsorption cannot reduce the level of total organic carbon (TOC) below 150 to 200 ppm (ref. 5). Therefore, if significant levels of organics remain in the wastewater after biological treatment and carbon adsorption, incineration of the wastewater to destroy these organics may be necessary. It should be emphasized that incineration is necessary if these organics are toxic. At this time there are no data concerning the toxicity of these organic constituents.

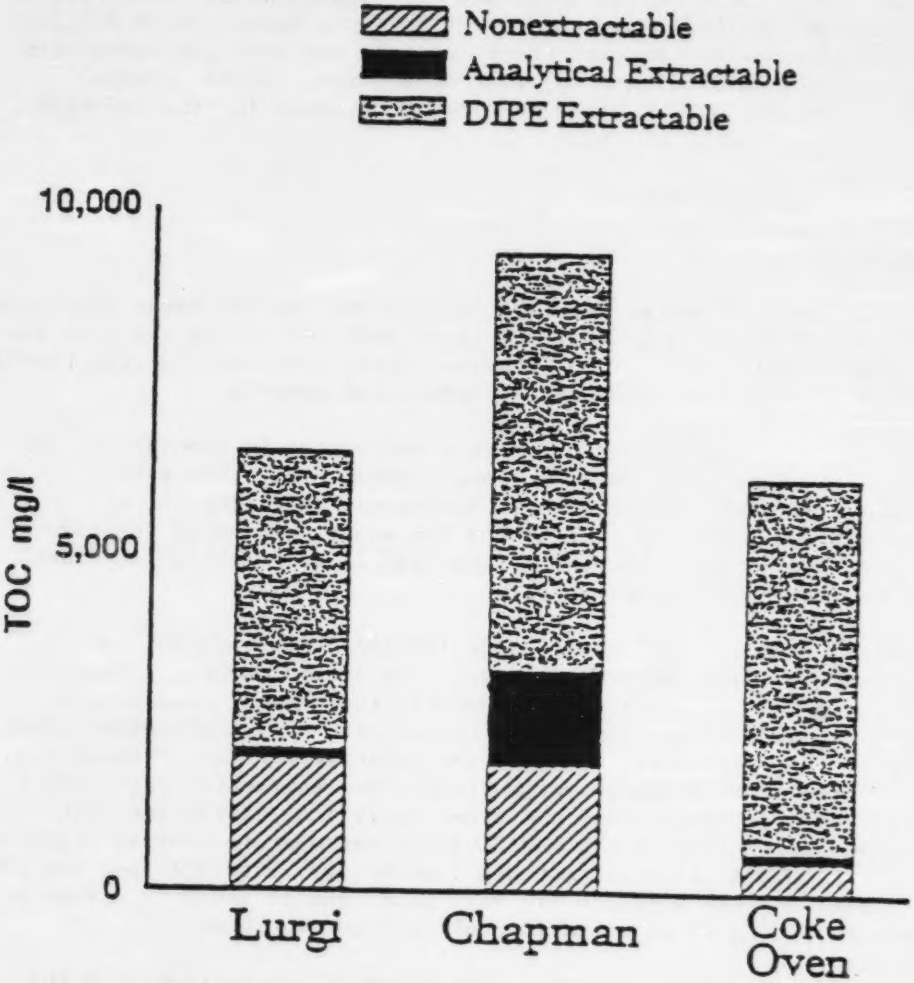

Figure 3. Extractable and Nonextractable Organics in Gasification and Coke Oven Wastewater (Ref. 5)

By-Products: Tar, Oil, Naphtha and Phenol

The composition of the by-products (tar, medium oil, naphtha and phenol) will affect their end use. Chemical analysis data for Kosovo by-products are shown in Table 7. Analysis of the phenol is not reported because a sample was not obtained during the test. Table 7 indicates that the sulfur contents of the liquid by-products become progressively higher in the "lighter" fractions. In contrast, the trend in the nitrogen values is reversed. These data indicate that heavy hydrocarbon by-products similar to those generated at Kosovo, could be used to satisfy some of the on-site fuel needs (e.g., for steam generation) of a U.S. Lurgi plant without flue gas desulfurization. This assumes that current SO_2 emissions standards consistent with those for large fossil fuel fired steam generators are applicable.

Table 7 also shows that the naphtha by-product contained none of the heavy polynuclear aromatics (PNA's) found in the tar and medium oil. Use of the tar and oil as fuel would destroy those PNA's by combustion. However, the naphtha could be used as a chemical feedstock with minimal risk of worker exposure to heavy PNA's.

CONCLUSIONS AND RECOMMENDATIONS

The conclusions and recommendations derived from the results of the Kosovo test program and from an assessment of the pollution control processes to treat key discharge streams from a Lurgi-based plant are presented in four areas:

- availability of controls,
- applicability of controls,
- integrated plant concerns, and
- discharge stream variability

AVAILABILITY OF CONTROLS

Pollution control processes for all of the key discharge streams are commercially available. Most of these processes have been proven in related industries (e.g., coke oven, refinery, etc.).

APPLICABILITY OF CONTROLS

Even though pollution control processes are commercially available, minor and trace components in discharge streams from gasification plants will affect the operation of those processes. Because many of these components are unique to gasification technology, direct transfer of pollution control process design from other industries may not be applicable.

INTEGRATED PLANT CONCERNS

Pollution control costs will be a significant portion of the base plant cost. The control of discharge streams by recycling or process modification should be considered in the total plant design, especially if significant cost savings for pollution control can be realized.

TABLE 7. CHEMICAL AND PHYSICAL DATA FOR KOSOVO BY-PRODUCTS

By-Product	Light Tar	Medium Oil	Naphtha
Specific Gravity (g/cm^3)	1.06	0.97	0.85
Higher Heating Value (kcal/kg)	8910	9500	9940
Lower Heating Value (kcal/kg)	8280	9400	8925
Ultimate Analysis (wt. %)			
Carbon	82	82	86
Hydrogen	8.4	8.9	9.9
Nitrogen	1.3	1.00	0.18
Sulfur	0.49	0.83	2.2
Ash	0.22	0.03	---
Oxygen (difference)	7.8	8.2	2.2
Moisture Content (wt. %)	1.1	0.8	---
PNA Analysis (mg/kg)			
Benz(a)anthracene	490	160	NF
7,12-dimethylbenz(a)anthracene	1100	62	NF
Benzo(b)fluoranthrene	310	120	NF
Benzo(a)pyrene	210	68	NF
3-methylcholanthrene	26	NF	NF
Dibenz(a,h)anthracene	23	6.6	NF
252 Group (as BaP)	950	280	NF

NF = not found.
--- = no data available.

DISCHARGE STREAM VARIABILITY

Every Lurgi-based plant will have unique discharge stream characteristics resulting from differences in coal feedstock properties, process operation, and plant configuration. Pollution control processes must be designed to handle worst case transients as well as "normal" operating conditions. Therefore, during the testing phase to obtain operating parameters on a specific coal feedstock, characterization of discharge streams during steady-state and transient conditions should be performed to define the bases for pollution control process design.

As stated previously, pollution control technology is available for Lurgi-based gasification plants, but the application of this technology is not completely straightforward. For this reason, pollution control process designs must be based on design data obtained over a broad spectrum of operating conditions. It is particularly important that data be obtained under both transient as well as steady-state conditions.

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ENVIRONMENTAL ASPECTS OF THE GKT COAL GASIFICATION PROCESS†

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INTRODUCTION

Thermal Conversion of coal is always accompanied by the production of pyrolysis products, of solid wastes like ash, slag or flydust, of different sulfur compounds and a number of undesired trace compounds in the gas. Quality and quantity of these components depend on the applied process principle, the composition of the reactants and on the main process parameters like temperature and pressure. The high temperature entrained coal gasification process according to GKT, a well established commercial process since 3o years, offers a coal conversion system with minimum environmental impact.

To evaluate the operating conditions and the environmental impact when gasifying American coal, TVA and GKT agreed to conduct a large scale test with about 5ooo short tons of Illinois No. 6 coal in a commercial coal to ammonia plant in Greece. TRW, funded by TVA, cooperated in the extensive test programme regarding the environmental aspects. The favourable results of the test runs, carried out in March/April 1981, and the extraordinary low environmental impact demonstrated, have led to TVA's decision to built its Murphy Hill plant basing on GKT's technology.

THE GKT PROCESS

In 1936/42 Friedrich Totzek and his coworkers developed a new gasification principle, the gasification of pulverized coal in an entrained bed reactor, using oxygen and steam as gasification media.

In this GKT PROCESS coal dust and oxygen are reacted within one second in a flame reaction to carbon monoxide and hydrogen, at close to atmospheric pressure and temperatures of 1400 to 1600 °C. Under these conditions, the coal ash converts to liquid slag and flyash.

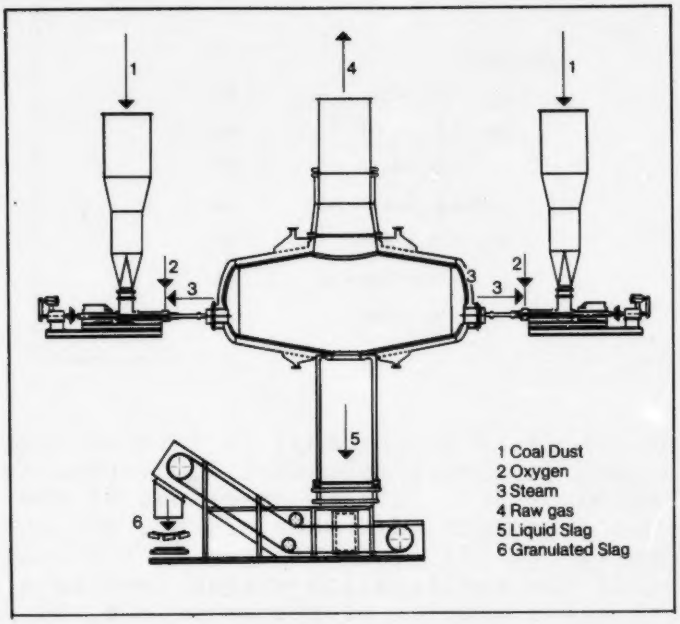


Figure 1 The GKT gasifier

The reaction vessel is shown in Figure 1. Coal dust metered via dosing screw conveyors, is injected with oxygen and steam through opposite burners. Liquid slag accumulating at the reactor wall, flows down through the bottom opening into a water bath, granulates and is discharged via chain conveyor. The reactor wall is cooled by raising steam in the double-wall jacket. The product gas exiting at the top is quenched to about 1000 °C by water injection in order to solidify slag droplets before entering the waste heat boiler.

The reactions of the coal with the gasifying agents are summarized in Table 1. Most important are Reactions (1) to (3) which lead to a product gas with approximately 90 % CO and H_2 at a ratio of 2/1 to 2.5/1. Formation of methane, Reaction (4), is of no importance at the high gasification temperatures. However, traces of methane are always present in the gas.

TABLE 1 REACTIONS OF THE SYSTEM C/H/O/N/S

Gasification reactions:

$$\mathrm{C + O_2 = CO_2} \tag{1}$$

$$\mathrm{C + CO_2 = 2\,CO} \tag{2}$$

$$\mathrm{C + H_2O = CO + H_2} \tag{3}$$

$$\mathrm{C + 2\,H_2 = CH_4} \tag{4}$$

Side reactions:

$$\mathrm{C + 2\,S = CS_2} \tag{5}$$

$$\mathrm{CO + S = COS} \tag{6}$$

$$\mathrm{H_2 + S = H_2S} \tag{7}$$

$$\mathrm{2\,CO_2 + S = SO_2 + 2\,CO} \tag{8}$$

$$\mathrm{3\,H_2 + N_2 = 2\,NH_3} \tag{9}$$

$$\mathrm{C + NH_3 = HCN + H_2} \tag{10}$$

$$\mathrm{O_2 + N_2 = 2\,NO} \tag{11}$$

The sulphur contained in the coal in form of organic and inorganic compounds, is almost completely converted to H_2S and COS at a molar ratio of 9/1. Further reactions of the system C/H/O/S permit the formation of traces of CS_2, SO_2 and elemental sulfur, reactions (5) to (8). The nitrogen in the coal and the nitrogen content of the gasification oxygen lead by a number of side reactions to the formation of traces of HCN, NH_3 and NO, reactions (9) to (11).

The reactions shown in Table 1 represent the minimum number which describe the system. Their combinations result in a large number of heterogeneous and homogeneous reactions occuring simultaneously.

Besides these reactions, also coal ash components will react under the prevailing conditions.

The coal ash contains practically all chemical elements in small traces, similar to all natural ores and minerals used for industrial purposes. Under gasification conditions accordingly many trace element side reactions as reduction reactions, volatilization reactions, so-called transport reactions and condensation reactions are experienced.

SYNTHESIS GAS VIA THE GKT PROCESS

The flow diagram of a GKT coal gasification plant for the production of synthesis gas is shown in Figure 2. All important streams entering and leaving the plant are marked.

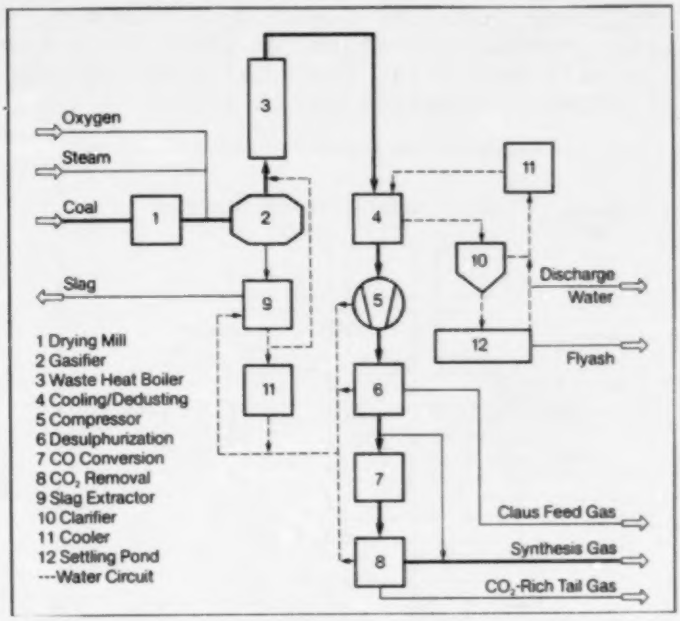

Oxygen
Steam
Coal
Slag
1
2
3
4
5
6
7
8
9
10
11
11
12
Discharge Water
Flyash
Claus Feed Gas
Synthesis Gas
CO_2-Rich Tail Gas
1 Drying Mill
2 Gasifier
3 Waste Heat Boiler
4 Cooling/Dedusting
5 Compressor
6 Desulphurization
7 CO Conversion
8 CO_2 Removal
9 Slag Extractor
10 Clarifier
11 Cooler
12 Settling Pond
---Water Circuit

Figure 2 Flowsheet of a synthesis gas from coal plant

The raw coal entering the plant is crushed and pulverized to the necessary particle size (< o.1 mm) and is simultaneously dried in a mill. The coal dust is pneumatically conveyed to the feed bunkers of the individual gasifiers. With oxygen and steam admixture the coal dust is injected into the gasifiers and gasified autothermally.

The slag leaving the reactor at the bottom is quenched in the water seal of the gasifier and discharged as a granulate. The raw gas after quenching is cooled to about 300°C in a waste heat boiler, where saturated steam at 1oo bar is raised.

Cooling of the raw gas to ambient temperature and compressor grade dedusting is attained in a series of steps comprising a washer cooler, a disintegrator stage and a wet electrostatic precipitator. The flyash and the sensible heat are absorbed by the wash water which is recycled via a clarifier and a cooling stage. The flyash is pumped as a slurry from the clarifier to a settling pond.

The cooled and dedusted raw gas is compressed to 2o-6o bar for desulphurization by a chemical or physical wash, a CO shift conversion and a CO_2 removal. According to the application of the synthesis gas the sulfur free gas is partly or totally entering the CO shift reactor and the CO_2-removal stage.

THE TEST UNIT

For the large-scale test operation the fertilizer plant of "Nitrogenous Fertilizer Industry S.A." in Ptolemais, Greece, was chosen. This plant started operation in 1963. Extentions increased production in 1971 and 1973. The coal gasification section of this plant is shown schematically in Figure 3.

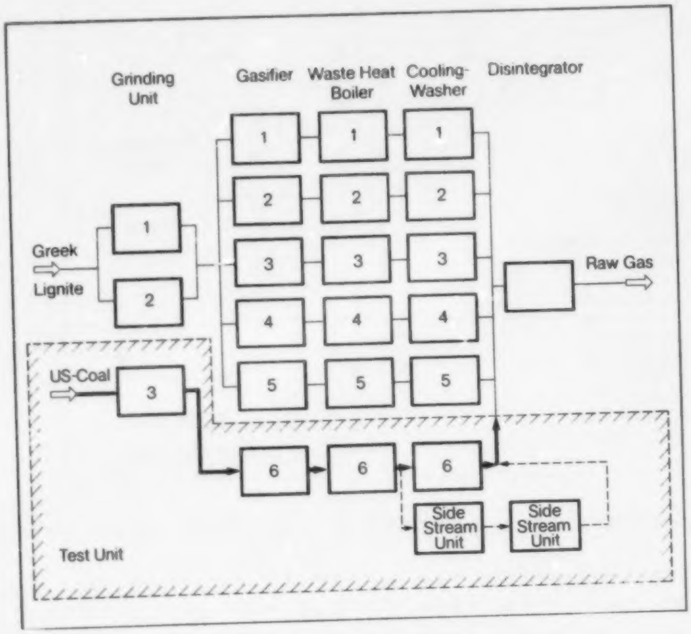

Grinding Unit
Gasifier
Waste Heat Boiler
Cooling-Washer
Disintegrator
Greek Lignite
US-Coal
Raw Gas
1
2
3
4
5
6
Side Stream Unit
Side Stream Unit
Test Unit

Figure 3 The Test unit at the NFI plant

Three grinding units and six gasifiers are available. For the test operation

- the drying and grinding unit no. 3 and
- the gasifier no. 6

of the plant were required.

From Figure 3 the limitations of the system are apparent. The raw gas produced in the test gasifier is mixed with the gas produced in the other gasifiers before entering the second washing stage. The washing water entering the cooling washer is recycle water from the operation of the total gasification and gas cleaning section of the plant.

For the determination of the chemical composition of the washing water in a scrubbing system not affected by the parallel operation of the gasifiers 1 to 5 with Greek lignite a wet gas cleaning side stream unit including

- a washer cooler
- a Theisen disintegrator
- a drop separator and
- a closed water circuit with clarifier and cooler

was installed, Figure 4.

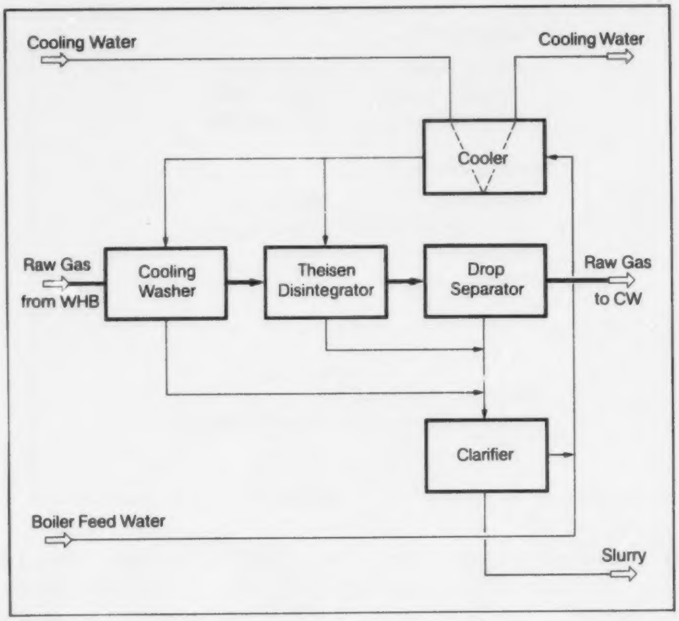

Cooling Water
Cooling Water
Cooler
Raw Gas
from WHB
Cooling Washer
Theisen Disintegrator
Drop Separator
Raw Gas
to CW
Clarifier
Boiler Feed Water
Slurry

Figure 4 The side stream gas cleaning unit

TEST RESULTS AND DISCUSSION

The following discussion will focus on the streams which are shown in Figure 2.
Especially

- the coal feedstock
- the slag
- the flydust
- the wash water from the washing unit and
- the raw synthesis gas before entering the compression stage

will be discussed.

Further streams, as

- the final synthesis gas
- the sulfur rich Claus gas and
- CO_2-rich off gas from the CO_2-removal stage

will be characterized.

TABLE 2 TEST GASIFICATION DATA

Operating Conditions	
Illinois No. 6 coal	6,300 kg/h
O_2/Coal (maf)[1]-ratio	1.06 kg/kg (maf)
Steam/Coal (maf)-ratio	0.11 kg/kg (maf)
Operating Results	
Raw gas (dry)	10,900 m_n^3/h
(CO + H_2)/coal(maf)-ratio	1.73 m_n^3/kg (maf)
Coal conversion: ηc	94.6%
Efficiency: $\eta_{th,\ chem}$[2]	77.8%

1.) maf = moisture and ash free

2.) excluding steam production in waste heat boiler

For orientation operational conditions and results are summarized in Table 2. The flow rates of all product and discharge streams are presented in Table 3. All the results presented are obtained at these test conditions.

The composition of the coal gasified is given in Table 4. The Illinois no. 6 coal has a high sulfur content, a medium ash content and a low chlorine content of o.o5 to o.o7 %. The moisture content of the coal dust prepared for gasification is 1 %. The solid by-products, slag and flyash comprise the coal ash and the unconverted coal, their composition is shown in Table 5.

The slag, recovered from the gasifier in granular form is environmentally harmless as it has been fused at high temperatures. According to the high SiO_2-content it has a vitreous and dense structure. Traces of dissolved carbon are responsible for its black colour. Leaching tests according to the RCRA procedure demonstrate, that practically no priority pollutants are develo-

TABLE 3 SPECIFIC FLOW RATES

Flow Rates of Product and Discharge Streams
Basis: 1 t Illinois No. 6 Coal (moisture free):

Synthesis Gas	1730 m_n^3/t
Claus Feed Gas	71 m_n^3/t
CO_2-Off Gas	831 m_n^3/t
Discharge Water [1]	1.3 m^3/t
Flydust (dry)	120 kg/t
Slag	46 kg/t

---

[1] Side Stream Unit only.
Commercial Operation ~ 0.5 m^3/t

TABLE 4 COAL ANALYSIS

Ultimate Analysis, wt.-% mf		Ash Analysis, wt.-%	
H	4.6	Fe_2O_3	17.0
C	69.6	SiO_2	49.8
$S_{combustible}$	2.6	Al_2O_3	21.5
N	1.4	CaO	3.2
Ash	12.7	MgO	1.2
$O_{(by\ difference)}$	9.1	Na_2O	0.4
		K_2O	2.4
Total Sulphur	2.7	TiO_2	1.0
		P_2O_5	0.1
		SO_3	3.4

Amax Delta Mine, Illinois No. 6 Coal

TABLE 5 SLAG AND FLYDUST ANALYSES

Component	Concentration in wt.-% (dry)	
	Slag	Solids in Wash Water
C	0.2	32.9
Ash	99.5	66.3
S	0.3	1.3
Ash: SiO_2	50.1	49.3
$Al_2O_3 + TiO_2$	25.5	23.5
FeO	10.8	-
Fe_2O_3	4.5	16.8
CaO	3.9	3.6
MgO	1.2	1.2
Na_2O+K_2O	2.5	3.0
P_2O_5	0.1	0.1
SO_3	-	1.9

TABLE 6 SLAG LEACHING TEST

Element	Concentration in mg/kg		
	R C R A Extract P_H5	Neutral Extract P_H7	R C R A Standard
Ag	<0.01	<0.01	5
As	<0.4	<0.4	5
Ba	<0.01	<0.01	100
Cd	<0.007	<0.007	1
Cr	<0.04	<0.04	5
Hg	<0.0002	<0.0002	0.2
Pb	<0.05	<0.05	5
Se	<0.4	<0.4	1
NH_3		0.7	None 1)
SCN^-		<0.1	None 1)
COD		4.8	None 1)

1) No Standard Available

ped, Table 6. Values below the analytical detection limit are marked by the sign "smaller than" (<) in Table 6 and the following relevant Tables. Traces of NH_3 result from the adsorbed quench water. Limited washing during extraction by chain conveyers will reduce this contaminant further. The use of the slag for road construction or other applications is therefore principally possible.

The flyash entrained in the raw synthesis gas is removed in the wet washing and cooling stage of the process. The fine grain size, the unconverted carbon content and the water content from the wet cleaning operation hinder an economic application. Therefore it has to be deposited. The exposition to the high temperature of the gasification results in an inert material. The carbon content is mainly graphitized, volatiles are limited. A hydrogen content up to o.1 % was analysed. Leachable components from the flyash but also from the raw gas are transferred to the discharge water, which is an important stream from the environmental point of view, as it is necessary at least to discharge surplus water resulting from coal moisture and steam input into the gasification stage as well as quenching water used for raw gas cooling before entering the waste heat boiler.

TABLE 7 INORGANIC PRIORITY POLLUTANTS

Element	Concentration, mg/l	
	Boiler Feed Water	Wash Water to Clarifier
Antimony	<0.06	<0.06
Arsenic	<0.1	<0.1
Beryllium	-	<0.02
Cadmium	<0.007	0.015
Chromium	<0.015	<0.015
Copper	0.025	0.02
Lead	<0.1	<0.1
Mercury	<0.0002	<0.0002
Nickel	<0.03	0.06
Selenium	<0.5	<0.5
Silver	<0.01	<0.01
Thallium	<0.4	<0.4
Zinc	<0.005	0.29

The inorganic priority pollutants in the discharge water in comparison to the boiler feed water, that was used as make up water during the test operation, are shown in Table 7.

It has to be stated, that a small increase in nickel most probably results from the low pH-water attack on the steel piping and the clarifier material. The increase in zinc content possibly result from the volatilization of zinc traces in the coal and the transportation as gaseous $ZnCl_2$ to the washing system.

The analyses of the discharge water and the boiler feed water are given in Table 8.

TABLE 8 WATER ANALYSES

Components	Concentration in mg/l	
	Boiler Feed Water	Wash Water to Clarifier
pH	11.2	3.8
COD	9	118
Dissolved Solids	98	812
Cl^-	9	306
F^-	<0.1	37
NH_3	<1	120
CN^-	<1	1.7 - 6
SCN^-	<1	3
$S^=$	<1	1
$S_2O_3^=$	<1	83
$SO_3^=$	<1	11
$SO_4^=$	25	217

The main components needing further treatment are NH_4^+, CN^- and also the sulfur compounds in lower state of oxidation. Especially from the relatively high amount of sulfate ions it is evident, that the dissolved sulfur compounds are oxidized finally to the sulfate stage. The chlorine content in the coal is nearly totally transferred to the discharge water. In actual operation at the TVA plant the discharge water will be minimized to less than half of the amount of the water that was actually discharged at the "Test Unit". The resulting concentrations in the discharge water stream will increase accordingly. Ammonia and cyanide result from the earlier discussed gasification reactions and are transferred from the raw gas to the discharge water.

The washing effect for the trace components in the raw gas is limited, as is demonstrated in Table 9, which presents the raw gas analysis after the washing stage in the side stream unit.

The remaining impurities are removed in the downstream gas

TABLE 9 RAW GAS ANALYSIS

Main Components Vol.-% (dry)		Impurities mg/m^3_n (dry)	
CO_2	9.4	H_2S	13,896
CO	62.2	COS	2,653
H_2	25.6	CS_2	80
N_2+Ar	1.8	SO_2	18
		NH_3	19
		HCN	89
		NO	4
		Solids	50

TABLE 1o PRODUCT AND BYPRODUCT GASES

Components	Concentration in vol.–%		
	Synthesis Gas	CO_2-Off Gas	H_2S Claus Gas
CO_2	3	75.82	73.39
CO	28.48	0.02	1.32
H_2	67.52	0.02	0.08
N_2 + Ar	0.99	24.14	
CH_4	0.01		
H_2S		4 ppmv	22.21
COS			2.47
CS_2			0.09
HCN			0.19
Methanol		300 ppmv	0.25

handling stages. In the Rectisol unit, according to GKT's concept, H_2S, COS, CS_2 and also HCN are removed and transferred to the Claus unit for sulfur production. The components SO_2 and NO are virtually completely reduced to H_2S and N_2 in the gas treatment system. Remaining traces will be removed with condensates and waste water from the gas treatment stages.

These combined water streams are used for slag quenching and finally as raw gas quenching water before the waste heat boiler, Figure 2. From the CO_2 removal a CO_2-rich stream is generated, which is vented to the atmosphere. The final clean synthesis gas stream, the CO_2-rich off gas and the H_2S-rich Claus gas are characterized in Table 1o. According to calcula - ting results it seems possible to reduce the CO-content of the CO_2 off-gas by changing the flash conditions in the CO_2 removal stage to still lower values.

A further analytical effort was aiming for evaluation of the organic compounds present in the waste streams of the GKT PROCESS.

Table 11 shows the results obtained for the raw gas after cooling and washing. Practically no higher hydrocarbon than methane and this also at a rather low level were detected.

TABLE 11 ORGANICS IN RAW GAS

Components	Concentration ppmv
CH_4	10
$C_2H_4+C_2H_2$	<0.5
C_3H_6	<0.5
Benzene	<0.5
Toluene	<0.5
Xylene	<0.5
C_3H_8	<0.5
C_2H_4	<0.5
CH_3SH	<0.5
C_2H_5SH	<0.5

To collect organics in the hot raw gas before entering the washer group XAD resin traps were used. No resin sample contained sufficient extract to perform liquid chromatography. Infrared analysis of each gravimetric residue indicated no organics other than those found in the resin blank. Low resolution mass spectrometry revealed that elemental sulfur (S_8) was the only species not found in the blank, Table 12.

TABLE 12 ORGANICS IN GASIFICATION STREAMS

Components	Raw Gas before Washer	Wash Water to Clarifier	Slag	Solids in Discharge Slurry
	mg/m_n^3	mg/l	mg/kg	mg/kg
Oil/Grease		1.3		
Formate		<0.1		
Phenols		<0.001		
TCO[1]	1.6	<0.1	0.1	7.2
Grav.[2]	3.8	13.2	32.0	780
S_8 in Grav.	~98%	97.2%	94.4%	94.3%
TCO+Grav.[3]	1.7	0.4	1.9	52

1.) Total chromatographable organics

2.) Gravimetric organics

3.) Sulfur free

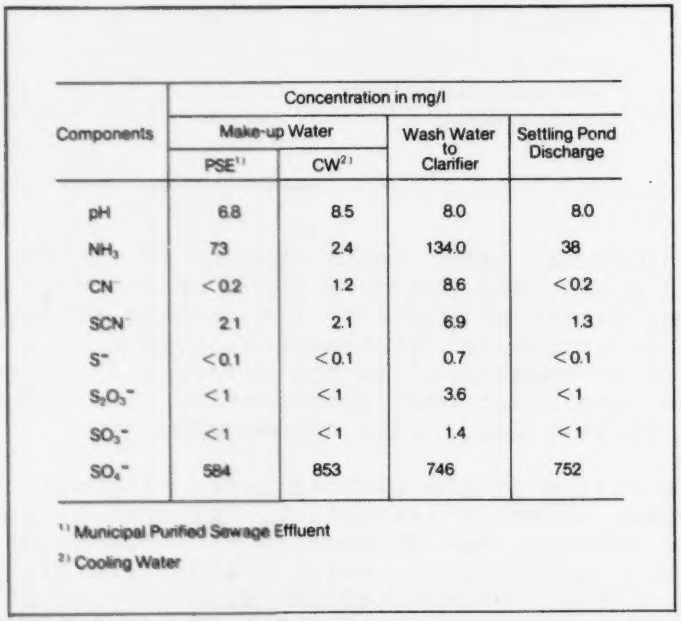
In the discharge water small amounts of formate are present and traces of grease and oil were found in the side stream washer system. Essentially all of the organic extracts of the sample could be attributed to elemental sulfur (S_8). No other organics could be identified in the extracts by infrared analysis and low resolution mass spectrometry. The resulting residue was insufficient for liquid chromatography.

Slag and solids in the washing water (flydust) were subjected to methylene chloride extraction, followed by gas chromatography on the extract. Low resolution mass spectrometry again indicated almost entirely elemental sulfur. The higher gravimetric residue of the flydust indicate also some organics with boiling points higher than that of the C_{16} normal alkane, which may result from the carbon content of the flydust, not fully graphitised, or dust fines, having passed through the filter.

CONCLUSIONS

From the results achieved it is evident, that special interest is directed towards the flydust slurry and the discharge water. The GKT concept for handling this streams is shown in Figure 2. The flydust slurry is transferred from the clarifier to a settling pond where it is slowly dewatered. The effluent from the pond is partly recycled to the main washing system. The surplus water in the system is discharged and will be treated further, especially for ammonia reduction. It has to be pointed out, that the impurities of the wash water react with each other and with the flyash. Sulfide ions are converted to $S_2O_3^{--}$ and SO_4^{--}. HCN reacts with sulfur compounds to form SCN^- and with the flyash to form insoluble complexes. Additional oxidation reactions occur in the settling pond. These oxidation reactions, which are catalysed by flyash components, involve $S_2O_3^{--}$, SO_3^{--}, CN^-, SCN^- and also NH_4^+. This experience is demonstrated in Table 13, which shows water analyses from the GKT coal gasification plant in Modderfontein, Republic of South Africa. This Figure, excluding the wash water stream to the clarifier, was presented by TRW and GKT in 198o.

TABLE 13 WATER ANALYSES FROM GKT COAL GASIFICATION IN MODDERFONTEIN,RSA



Components	Concentration in mg/l			
	Make-up Water		Wash Water to Clarifier	Settling Pond Discharge
	PSE[1]	CW[2]		
pH	6.8	8.5	8.0	8.0
NH_3	73	2.4	134.0	38
CN^-	< 0.2	1.2	8.6	< 0.2
SCN^-	2.1	2.1	6.9	1.3
$S^{=}$	< 0.1	< 0.1	0.7	< 0.1
$S_2O_3^{=}$	< 1	< 1	3.6	< 1
$SO_3^{=}$	< 1	< 1	1.4	< 1
$SO_4^{=}$	584	853	746	752

[1] Municipal Purified Sewage Effluent

[2] Cooling Water

The changes in composition from the wash water stream before the clarifier to the final water discharge stream from the pond are remarkable, no further treatment of the discharge water is carried out.

SOURCE TEST OF THE TEXACO GASIFICATION PROCESS[†] LOCATED AT OBERHAUSEN-HOLTEN, WEST GERMANY

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ABSTRACT

A comprehensive environmental characterization of water and solids from the Ruhrkohle/Ruhrchemie Coal Gasification Pilot Plant in Oberhausen-Holten, West Germany has been conducted. Coal is gasified at the plant with a modified Texaco coal gasification process. The pilot plant tests were conducted in November, 1980, during gasification of Illinois No. 6 coal. A test plan was prepared including stream selection, sample collection and chemical analyses. Multiple samples of six process water and four process solid streams were collected during two twelve-hour environmental balance periods. Normal pilot plant operation was maintained during the first period; the second incorporated water recycle to observe dissolved levels of components with minimized makeup water.

Samples of liquid and solid process streams have been subjected to comprehensive analyses including water quality parameters, trace elements, organic characterization, physical testing, radioactivity analyses and bioassay testing.

These efforts, conducted under contract with the Tennessee Valley Authority, have been performed to provide support information for both process operation and environmental impact associated with a 10,000 ton per day coal gasification plant proposed by TVA for a northern Alabama site. Topics to be addressed in the presentation include pilot plant configuration and operation, sample collection, analytical testing and results of the characterization program.

ENVIRONMENTAL TEST RESULTS FOR THE RUHRKOHLE/RUHRCHEMIE/COAL GASIFICATION PILOT PLANT

Under a contract with the Tennessee Valley Authority, Radian Corporation has performed a comprehensive environmental characterization of the process water, effluent water and solid waste from the Ruhrkohle/Ruhrchemie Coal Gasification Pilot Plant in Oberhausen-Holten, West Germany. At this plant, coal is gasified with a modified Texaco coal gasification process.

During a recent test in November and December, 1980, samples of process water streams, effluent water streams, slag, raw coal and coal slurry were collected. The samples were obtained during two 12-hour environmental balance periods on November 14 and November 18, 1980.

The liquid and solid samples have been subjected to comprehensive analyses. Some analyses were carried out on-site at the Ruhrchemie plant in Oberhausen-Holten while others have been performed at the Radian laboratories in Austin, Texas.

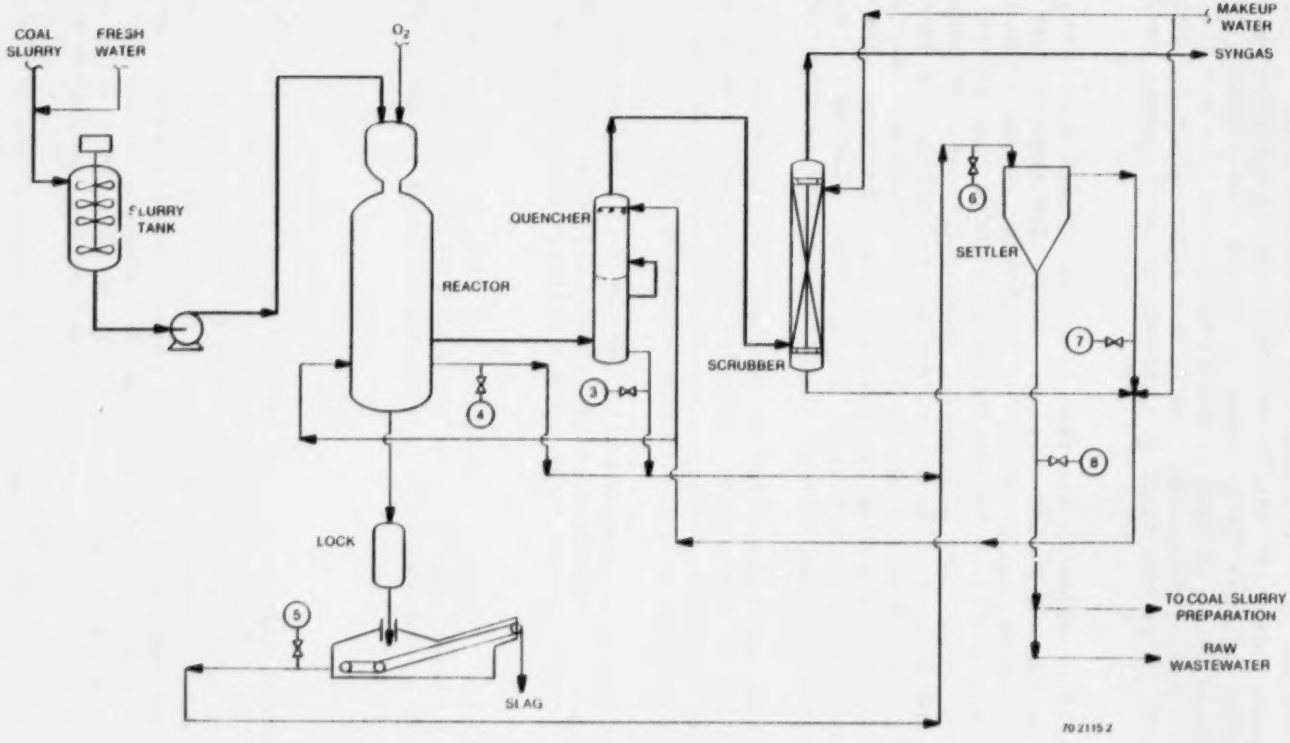
Some of the results of the program are briefly summarized in this paper. The process is described and the overall mass balance is presented. Many of the key characteristics of the process effluent water are defined, and some of the results from the wastewater treatability study are presented. The solid wastes from the process were subjected to RCRA leaching tests, and these results are given.

PROCESS DESCRIPTION

The testing took place at the Ruhrkohle/Ruhrchemie demonstration coal gasification plant located in Oberhausen-Holten, West Germany. This plant contains a Texaco gasifier and has a nominal coal capacity of 5,700 to 6,100 kg/hr [150-160 tons/day]. A simplified flow scheme of the Ruhrkohle/Ruhrchemie demonstration plant is shown in Figure 1. The numbered points on this diagram identify the locations from which solid and liquid samples were taken during the environmental balance periods.

In the plant, coal is fed from a storage bunker to a grinding mill. There it is pulverized and combined with fresh water or, alternatively, effluent water recycled from the settler. The resulting coal slurry is pumped to agitated run tanks and from there into the gasification reactor.

The Texaco Coal Gasification Process reactor is a pressurized, entrained bed, downflow slagging gasifier. It operates under pressures of 2 to 10 Mpa [300 to 1,500 psia] and at high temperatures, generally in the range of 1,200 to 1,400°C. These temperatures are above the melting point of the coal ash.


COAL SLURRY
FRESH WATER
SLURRY TANK
O$_2$
REACTOR
QUENCHER
SCRUBBER
SETTLER
LOCK
SLAG
MAKEUP WATER
SYNGAS
TO COAL SLURRY PREPARATION
RAW WASTEWATER
③
④
⑤
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⑦
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70 2115 2

FIGURE 1. FLOW SCHEME FOR THE RUHRKOHLE/RUHRCHEMIE COAL GASIFICATION PLANT DURING THE ENVIRONMENTAL TESTING

The coal slurry and oxygen are fed into the top of the gasification reactor vessel. This vessel is lined with refractory, and it consists of two zones, a gasification zone and a radiant zone. The basic combustion and gasification reactions occur in the gasification section. The raw synthesis gas from the gasification section passes into the radiant cooler or quench section of the vessel. Here the gas is partially cooled and process steam generated. Synthesis gas from the gasifier is routed into a quench tower, where recycled process water is used to additionally cool the gas and remove particulate matter. The synthesis gas leaves the quench tower and passes into a water scrubber where the final gas cooling and particulate removal takes place.

Most of the slag produced in the reactor is solidified in a water bath in the bottom of the radiant cooler section. It is then removed from the reactor through an electronically-controlled lockhopper system. The slag and sluice water fall into a covered bin where the granulated slag is continuously removed by a conveyor belt. The slag water, containing some fine particulates, is sent to the settler. The water from the radiant cooler section of the gasifier and from the quench tower is routed to a flash tank where dissolved gases are flashed off during depressurization. The water from the flash tank then passes into the settler. The residence time in the settler is sufficient to allow settling of most of the fine particulate matter.

Two water streams are taken from the settler. The overflow water stream, taken off near the top of the settler, contains a relatively low concentration of solids. The underflow stream, taken from the bottom of the settler, contains the residual fines at a much higher concentration.

The settler overflow is combined with the scrubber blowdown stream and makeup water stream. This combined water stream is used as slag sluice water and also recycled to the quench tower and the radiant zone of the gasification reactor.

The underflow [or at least a portion of it] from the settler serves as the water blowdown stream from the coal gasification unit. The blowdown stream is first sent to an open holding tank before being routed to the plant water treatment system.

MASS BALANCES

The environmental balance periods took place on November 14, 1980 [EB-1] and November 18, 1980 [EB-2]. During the tests, Illinois No. 6 coal was processed at a rate of 6,900 to 7,200 kg/hr [180 to 190 tons/day]. The composition of the test coal is shown in Table 1. The major difference in the operating conditions between the two environmental balance periods was the disposition of the clarifier underflow [bottoms] stream. During the first environmental balance period [EB-1], all of the settler underflow stream was sent to the holding tank and then to water treatment; no underflow was recycled. During the second environmental balance period [EB-2], the fresh water requirements to the plant were minimized. Approximately half of the settler underflow stream was recycled to the coal slurry preparation area to satisfy the water requirements to slurry the fresh coal which was sent to the gasifier. The remainder of the settler underflow was sent to the plant water treatment facilities.

TABLE 1. COMPOSITION OF ILLINOIS NO. 6 COAL

Component	Concentration*
Ash	11.21
Volatile	28.54
Fixed Carbon	50.25
Energy Content [Btu/lb]	12686
C	70.94
H	4.94
N	1.28
Cl	0.05
S	3.37
Ash	11.21
Oxygen (difference)	8.21
	100.00

*Values as percent [%] except Energy Content

Some of the operating conditions, as reported by Ruhrkohle/Ruhrchemie for the environmental balance periods, are summarized in Table 2.

TABLE 2. OPERATING CONDITIONS DURING ENVIRONMENTAL BALANCE PERIODS

Solids Feed Rate, kg/hr	6,000-6,300
Carbon Conversion [Once-Through], %	89-95
Dry Syngas Production, NM^3/hr	11,800-12,200
[H_2+CO] Production, NM^3/hr	9,000-9,400

Total material balances for both environmental balance periods were developed. These are shown in Table 3. The balances [or closures] are quite good for both test periods. Ruhrkohle/Ruhrchemie reported material balances for oxygen, carbon, water, sulfur, and nitrogen. The oxygen, carbon, water, and sulfur balances closed within ±4%. The nitrogen balances were within ±7% of closure.

TABLE 3. RUHUKOHLE/RUHRCHEMIE COAL GASIFICATION PLANT - TOTAL MATERIAL BALANCE

	Stream Flow Rates, kg/hr			
	Environmental Balance Period 1		Environmental Balance Period 2	
	In	Out	In	Out
Coal Feed	7,157		6,923	
Water	8,312		4,600	
Other Inlet Streams	6,226		5,921	
Synthesis Gas		11,597		11,542
Effluent Water		7,708		3,706
Slag & Other Outlet Streams		1,863		1,833
TOTAL	21,695	21,168	17,444	17,081
Balance [Out/In], %	97.6		97.9	

WASTEWATER CHARACTERISTICS AND TREATABILITY

Samples of seven water streams were obtained during the two environmental balance periods. These streams were:

Inlet Streams - fresh water

Process Streams - gasifier quench water
- quench tower bottom stream
- slag water
- settler inflow water

Outlet Streams - settler overflow water
- settler underflow water

During the environmental testing, the settler overflow water stream was recycled to the process. The settler underflow stream served as a purge stream, and was sent to wastewater treatment. During the second environmental balance period, some of the settler underflow was recycled to the coal slurry preparation area.

Several hundred gallons of the pilot plant settler underflow stream were collected during the two environmental balance periods. Settler underflow water from the second environmental balance period was subjected to treatability tests in a screening study performed by AWARE, Inc., of Nashville, Tennessee. The goal of this screening study was to define the treatability of wastewater from the Texaco coal gasification process. A conceptual wastewater treatment system was simulated on a laboratory-scale in the study. This system utilized conventional existing water treatment technology. Bench-scale simulation of wastewater treatment processes is an accepted and often the only means of obtaining treatment system design criteria when a "new" industrial wastewater is involved.

In the study, each treatment process was individually simulated using a portion of the wastewater to determine optimum process conditions. After the optimum conditions for a process were defined, the remainder of the wastewater was treated at those conditions. The next treatment process in the sequence was then evaluated.

A summary of the water quality characteristics of the raw settler underflow water stream is presented in Table 4. The raw wastewater characteristics are either average values of samples taken from the drums of wastewater to be treated or the value of a composite of samples from the drums. The sulfide and cyanide concentrations had the greatest variations among drum samples. Sulfide results were biased low because the samples were hot when collected, and some off-gasing occurred during cooling.

TABLE 4. CHARACTERISTICS OF WASTEWATER TO TREATMENT

Parameter	Concentration [ppm]
COD	540
BOD	202
Phenolics	<0.018
NH_3-N	1,550±98
CN^-	15±14
SCN^-	11
$S^=$	128±80
$SO_4^=$	5
TSS @ 105°C	152±42
TDS @ 180°C	960
Alkalinity [as $CaCO_3$]	4,070
pH[units]	8.3

A relatively high ammonia concentration was observed in the raw wastewater samples. Minimal concentrations of nitrate or nitrite were found. The total alkalinity was found to be high. Bicarbonate alkalinity was the predominant form.

The wastewater treatability screening study was directed toward the reduction of the major wastewater quality parameters including BOD, COD, TSS, NH_3, and H_2S levels. The laboratory treatment system, consisting of conventional solids removal, steam stripping, and oxidation, was effective in reducing these parameters. The reductions are summarized in Table 5. The removal efficiency across the total treatment process for both COD and TSS was in the range of 70-80%. The removal efficiency for most other constituents was in excess of 90%. Total dissolved solids increased substantially due to caustic and acid additions required for pH adjustment during the treatment sequence.

TABLE 5. TREATABILITY RESULTS

Component	Reduction [%]
BOD	91
COD	68-86
TSS	67-86
NH_3	>99
H_2S	∿99
Fe	83
TDS	*
Sulfate	*
Arsenic	0
Fluoride	3
Selenium	0
Chloride	0

*The use of NaOH and H_2SO_4 for pH adjustment increased the levels of sulfate and dissolved solids.

The effect of the treatment process on the levels of various metals was also determined. Elements whose concentrations are reduced by the treatment system include Al, Ba, Be, Ca, Fe, Mg, Mn, Pb, Si, and Ti. On the other hand, the concentrations of several metals were virtually unaffected in the treatment process. Included in this category are As, B, Cd, Ni, Sb, and Se. The levels of a number of elements, including Ag, Co, Cr, Mo, Tl, and V, were below detectable limits in both the raw wastewater and the effluent from the treatment system.

SOLIDS CHARACTERIZATION

Two process solid wastes and two solid wastes from the bench-scale wastewater treatment system were subjected to RCRA extractions. The solid wastes were:

- process wastes - slag
  settler fines

- treatment wastes - primary sludge
  biosludge

An elemental analysis was performed on the RCRA leachates. The results of these analyses are shown in Table 6. None of the RCRA limits for metals was exceeded in the leachates of any of the solids stream.

TABLE 6. RCRA LEACHING RESULTS OF SOLIDS*

Element	Process Samples		Treatability Samples		
	Slag	Settler Fines	Primary Sludge	Biosludge	RCRA Limit
Ag	<0.001	<0.001	<0.001	<0.001	5.0
As	<0.003	<0.003	0.031	0.039	5.0
Ba	0.094	0.10	0.21	0.29	100
Cd	0.008	0.014	0.010	0.35	1.0
Cr	<0.001	<0.001	0.074	0.055	5.0
Hg	<0.0005	<0.0005	<0.0005	<0.0005	0.2
Pb	<0.002	0.024	0.003	0.008	5.0
Se	<0.004	<0.004	<0.004	0.078	1.0

*Concentration in μg/ml (ppm)

SUMMARY OF RESULTS AND CONCLUSIONS

Some of the major results and conclusions of this study are:

- The gasification pilot plant appeared to be operating at steady-state conditions during the environmental testing.
- The total mass balance showed very good closure.
- Existing conventional wastewater treatment technology is effective in reducing the significant effluent water quality parameters including BOD, COD, TSS, NH_3, and H_2S.
- The concentrations of many of the trace metals are significantly reduced in the wastewater treatment system.
- The quality of most receiving waters should not be adversely affected by the treated effluent if properly treated with existing wastewater treatment technology.
- The solid wastes are not classified as toxic wastes according to RCRA extraction procedures.

ACKNOWLEDGEMENT

The coal test run was sponsored by the Electric Power Research Institute and we wish to acknowledge the assistance which they provided during our sampling activities. We would especially like to express our appreciation and thanks to the staff and operating personnel at the Ruhrkohle/Ruhrchemie gasification plant for their considerable efforts in support of our sampling program.

The assistance and cooperation of the Texaco Development Corporation is gratefully acknowledged.

SOURCE TEST AND EVALUATION OF A RILEY[†] GAS PRODUCER FIRING NORTH DAKOTA LIGNITE

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ABSTRACT

A ten-foot six-inch diameter Riley Morgan gasifier was operated for 14 days to convert North Dakota lignite to low-Btu gas. During that period, the gasifier was operated at a range of load conditions, and the product gas was transported to a commercial-scale kiln burner mounted in a large combustion test chamber. Process stream conditions and compositions were recorded throughout the test and were submitted to an SAM/1A analysis. Gaseous effluent streams were found to be well controlled due to the unique Riley coal feed and poke hole systems. Solid wastes from the process (gasifier ash and cyclone dust) were found to be nontoxic, noncarcinogenic and nonmutagenic. Gasifier wastewater effluent (ash pan water) was similarly found to be nonhazardous. Although combustion stack gases were not monitored, sulfur and particulate loadings in the gasifier product gas indicated that the stack gases would comply with current EPA New Source Standards. If all reduced nitrogen compounds were converted to NO_x, however, these emissions would exceed New Source Performance Standards.

"SOURCE TEST AND EVALUATION OF A RILEY GAS PRODUCER FIRING NORTH DAKOTA LIGNITE"

In 1979, American Natural Service Company commissioned the Riley Stoker Company to perform a full scale test of the low Btu gasification of North Dakota lignite in the Riley coal gasifier. Co-sponsors of the test were the Riley Stoker Company, The Hanna Mining Company and the Environmental Protection Agency through a contract with Radian Corporation. This report summarizes the results of that test and more specifically the environmental assessment of the Riley gas producer carried out by Radian Corporation.

PROCESS DESCRIPTION

The Riley gasifier is a modern, modified version of the Morgan gas producer, workhorse of the steel, glass, lime, pulp and chemical industries during the first fifty years of this century. Of the nearly 1,100 of these first generation units manufactured, at one time installations could be found on every continent in the world.

Since 1974, Riley Stoker Corporation has been operating a commercial sized demonstration unit at its Worcester, MA., R & D facility, the primary goal being the refinement of the successfully established first generation technology to the standards imposed by both environmental and operational constraints of the synfuels industry. A secondary, but no less important goal, has been the gaining of hands on experience in an area long treated as more an art than a science, and in which hard data is generally lacking.

During this time, a total of twenty-two demonstration runs with various eastern coals was carried out on the gasifier, together with an equal amount on a smaller one-fifth scale gasifier. Results of this program, together with a summary of practical operating experiences have been presented before other bodies (References 1, 2, 3).

THE GASIFIER

The Riley gasifier is depicted in Figure 1. This unit is an example of that group of gas producers classified as thin-bed, atmospheric. The entire fuel bed, including ash, never exceeds 140 cm. (55 inches), and slowly rotates, at a speed of one revolution in six and one-half minutes.

The height of the active fuel bed, 76 to 91 cm. (30-36 inches), differentiates this gasifier from moderately deep bed gasifiers (Wellman-Galusha, Lurgi), and very deep bed gasifiers (two-stage units). This design resulted from the need to accommodate swelling bituminous coals in the steel

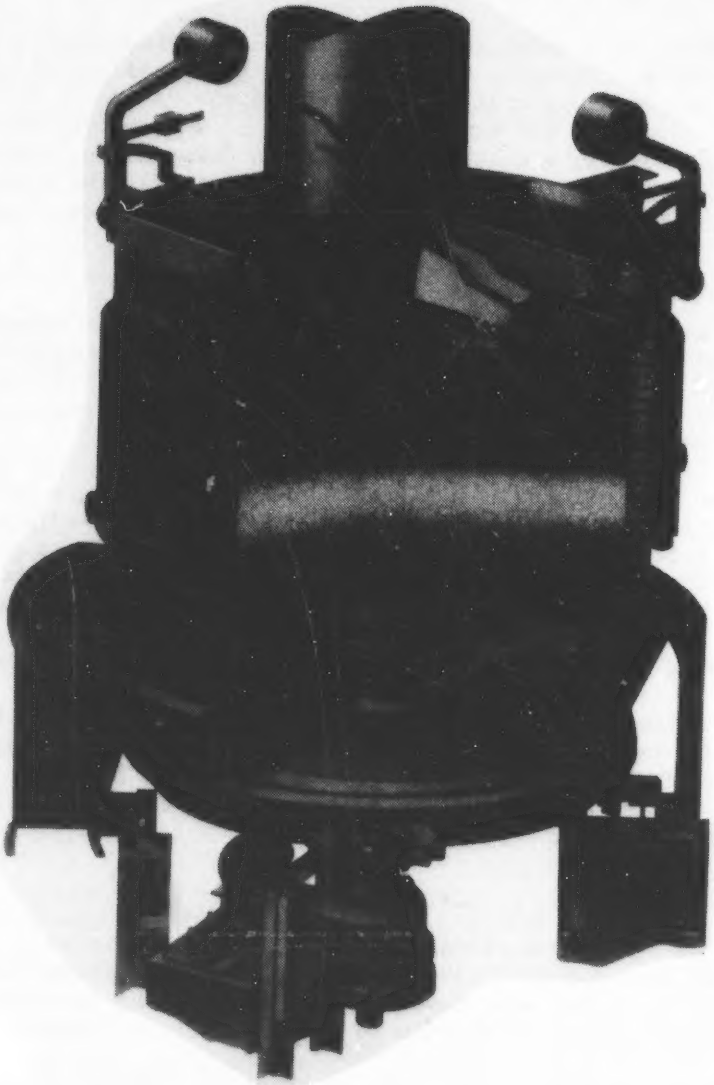

Figure 1. The Riley Gasifier

industries of the United States and the United Kingdom.

As has been found (Reference 1), coal particle heating rate is the controlling factor in managing swelling coals, and the ability to vary bed height allows the time-temperature history of the individual coal particle to be preselected and governed, resulting in minimal swelling. In general, thin-bed gasifiers operate with considerably higher exit temperatures than do the other classes of gasifiers, so that the distillation/pyrolysis environment which is first seen by the coal is more severe. This difference must be kept in mind in comparisons of yields and distribution of some of the minor families of compounds evolved from different gasifiers. Ash retention characteristics may also be influenced.

Continual rotation of the entire 3.2 meter (10'-6") I.D. unit accomplishes a number of purposes. Primarily, it is to assure even coal distribution across the entire fuel bed, a crucial factor in thin-bed management. This is accomplished without the use of an internal distributor by means of a slot drum feed across an entire radius of the unit. Thus, a continuous curtain of the fuel is evenly laid upon the advancing fuel bed.

Second, two horizontally fixed but vertically moveable water-cooled bars perform the function of fuel bed agitation, another requirement for swelling coals.

Third, ash is removed intermittently thru the use of a plow mechanism which is periodically stopped, scooping ash from the integral pan and discharging it over the ash pan lip. Some of the seal water will be carried over with this ash, and means for its treatment must be considered.

The Riley gasifier utilizes a blast hood for air/steam admission, rather than a grate, the ash bed acting as the diffuser.

THE SYSTEM

The demonstration facility at Riley Stoker is shown schematically in Figure 2. Coal is fed to the unit from a 60 ton nitrogen sealed bunker thru a three-valve lock hopper system, and is gasified by the countercurrent air/steam mixture. Gas exits thru a .9 meter (36 inch) insulated line, is cleaned of particulate in a high efficiency cyclone and transported to a 300 million Btu/hour test furnace where it is combusted. Char is removed from the cyclone dry, thru a lock hopper arrangement. A photograph of the installation is shown in Figure 3.

DESIGN FOR EMISSIONS

Much of the work at RSC during the past seven years has been devoted to design improvements of those parts of the system responsible for fugitive emissions. Historically, most gas producer manufacturers paid scant attention to the two areas most responsible for such emissions of raw gas: the coal feed system and access ports.

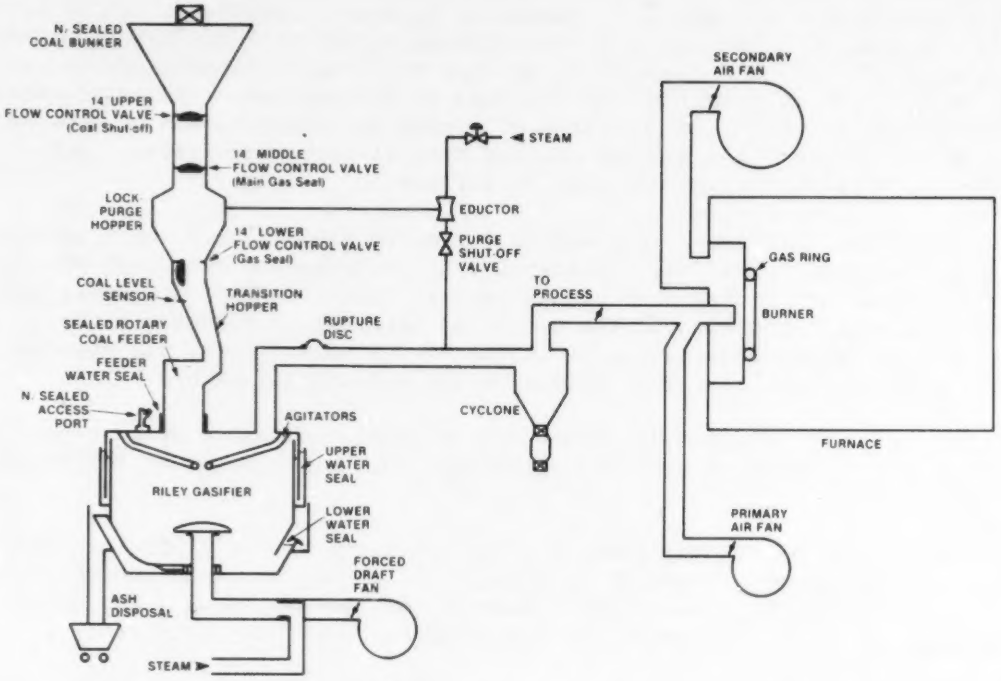
N. SEALED COAL BUNKER
14 UPPER FLOW CONTROL VALVE (Coal Shut-off)
14 MIDDLE FLOW CONTROL VALVE (Main Gas Seal)
LOCK PURGE HOPPER
14 LOWER FLOW CONTROL VALVE (Gas Seal)
COAL LEVEL SENSOR
TRANSITION HOPPER
SEALED ROTARY COAL FEEDER
FEEDER WATER SEAL
N. SEALED ACCESS PORT
RUPTURE DISC
AGITATORS
UPPER WATER SEAL
RILEY GASIFIER
LOWER WATER SEAL
FORCED DRAFT FAN
ASH DISPOSAL
STEAM
STEAM
EDUCTOR
PURGE SHUT-OFF VALVE
TO PROCESS
CYCLONE
SECONDARY AIR FAN
GAS RING
BURNER
FURNACE
PRIMARY AIR FAN

Figure 2. Schematic of the Test Facility

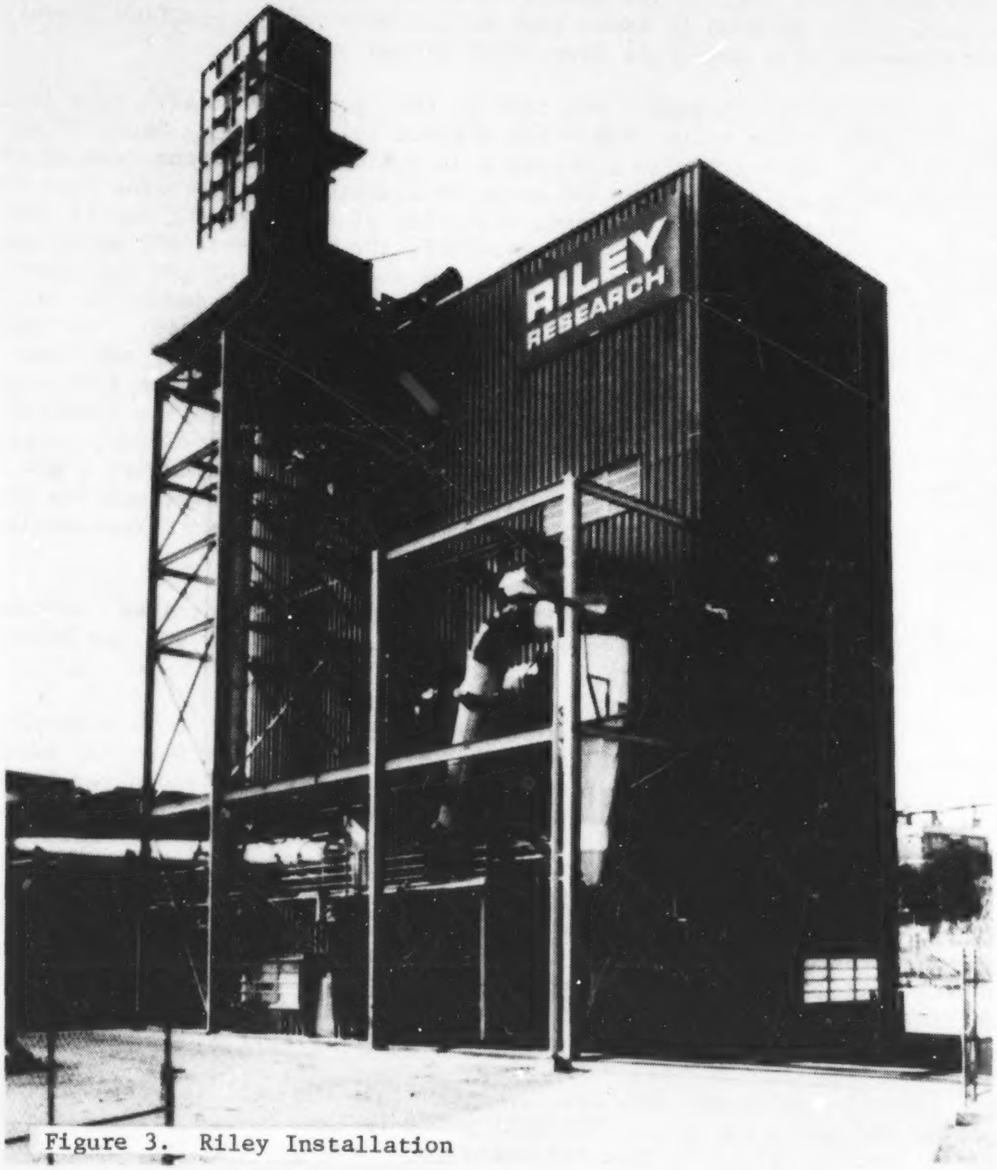
RILEY
RESEARCH

Figure 3. Riley Installation

Coal Feed System

In the Riley Stoker lock-purge coal feed system as shown in Figure 2, fuel is inventoried up to a level just below the middle valve, with the valves positioned as shown. The top valve must support a head of coal up to 6.4 meters (21 feet). The middle valve is closed to contain system gases. The lower valve is open to admit lock hopper coal to the gasifier feeder. All valves are of a semi-ball type, with ground seats.

As gasification proceeds the fuel in the lock hopper falls to a level just below the lower valve, where its absence is detected by means of a sonar device. This triggers a sequence as follows: following closure of the lower valve, a short burst of steam is admitted into the line from the eductor to the lock hopper cleaning that line of any residual tar or dust from the previous cycle. After an interval, the purge shut-off valve opens, and the steam eductor begins evacuating the lock hopper of gas and discharging it into the downstream gas piping system. The pressure in the lock hopper eventually becomes sub-atmospheric (660 mm. Hg. or less). At this time, the steam and purge shut-off valves close, and the upper two flow valves open, admitting coal from the main storage bunker to the lock hopper. These valves remain open until the lock hopper is filled to the previous level (approximately 1 ton). At this time the upper valve closes, interrupting coal flow, followed by the middle valve closing, creating a gas tight seal. The lower valve opens with middle valve closure, and the cycle is completed. Total elapsed time for this entire cycle is approximately one minute.

Throughout this sequence, gasifier feed has been maintained continuously, from the inventory of coal located between the coal feeder and the lower lock valve.

By the maintenance of a nitrogen blanket just slight above atmospheric pressure in the storage bunker above this system, together with the eductor system, migration of gases is always toward the gasifier, and never from it.

Access Ports

After a number of trials, RSC has perfected a nitrogen-sealed (any inert will do), universal joint access port, to be used during those times when access to the gasifier bed is a necessity. This unit is shown in Figure 4. Mounted atop a machined ball that moves within a gland seal fixed to the gasifier deck is another ball valve, a packing gland and a flexible hose conveying inert gas at approximately 1.4 kg/cm^2 (20 psig).

Insertion of a rod thru the upper gland to the ball valve is followed by opening the inert gas line. The ball valve is then opened and the rod inserted into the gasifier thru the assembly, inert gas flowing into the gasifier, and also around the upper gland to the environment.

This arrangement assures no leakage of producer gas into the environment,

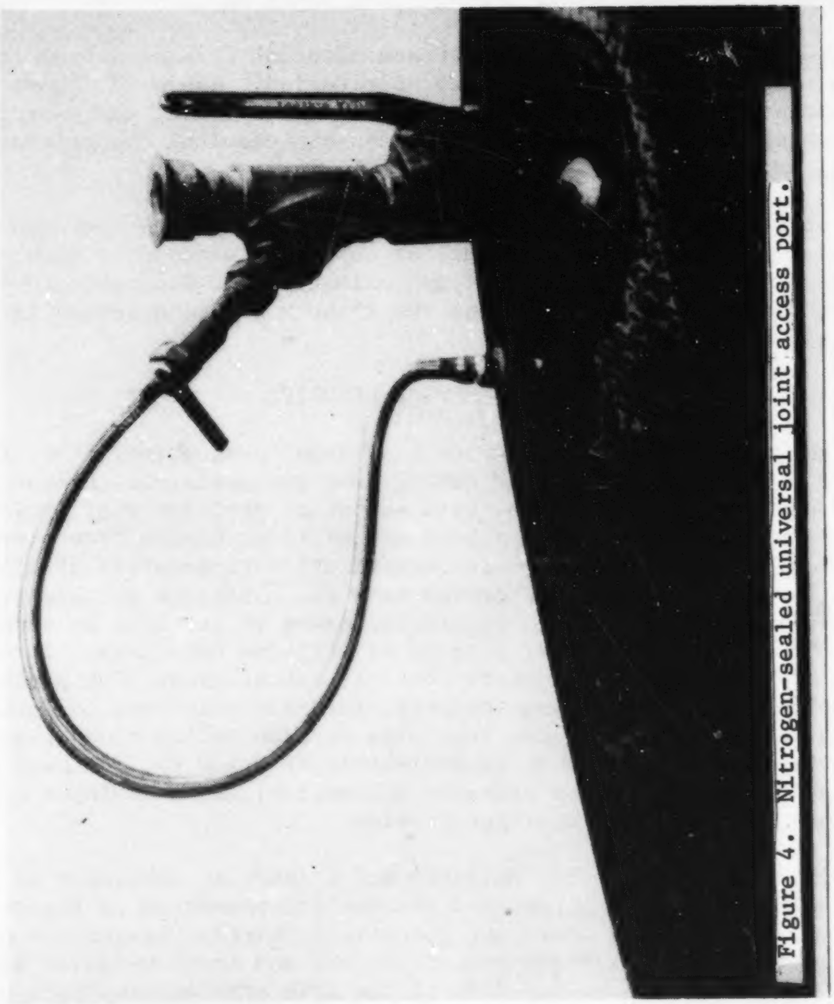

Figure 4. Nitrogen-sealed universal joint access port.

and also makes possible viewing of the fuel bed by the substitution of a plexiglass plate for the rod or other device.

ABSTRACT OF RUN

The gasifier test facility was operated from December 4 to 15, 1979. During this period a total of 374 metric tons of North Dakota lignite was gasified. Because of some non-gasifier problems, two interruptions caused shutdowns early in the test. The major portion of the test fuel was processed in the last five days of operation, and the results presented herein represent data taken from this continuous period. More specifically, data for the environmental assessment were taken over a 25 hour period extending from 0900 hours on December 13 through 1000 hours December 14.

Tables 1 and 2 present the heat and material balance around the gasifier at a time near the end of the 25 hour period. Table 3 shows a summary of the concentrations of the major species of the product gas over the 25 hour operating period. Table 4 summarizes the chemical compositions of the feed coal, tar and cyclone dust.

Over the total two week test period, the gasifier was operated at feed rates up to 4550 Kg/hr (10,000 lb/hr) of coal, and produced a high quality low Btu gas with a heating value of approximately 160 Btu/cubic foot. A summary of process conditions during the 25 hour sampling period is given in Figures 5 and 6.

ENVIRONMENTAL RESULTS

For the purposes of a source analyses model evaluation, five effluent or process streams are considered coming from the gasifier: product gas vapors; product gas particulates, tars and oils; gasifier ash; cyclone dust; and ash pan water. Product gas vapors are distinguishable from product gas particulates, tars and oils by a characterization temperature of 115 C (240 F). The product gas is separated into two fractions at this temperature by the sampling procedure. The separation makes it possible to assess the potential health and ecological effects of fugitive emissions. It also allows an evaluation of appropriate control technologies. The phase condensed and collected at 115 C (particulates, tars and oils) was collected in an electrostatic precipitator. The remaining portion of the product gas (vapors) was collected in a condenser at approximately 15 C (60 F), followed by an organics absorption resin for organics collection, or an impinger train for trace elements, ammonia or hydrogen cyanide.

The results of the source analysis model (SAM/1A, Reference 4) evaluation of the five effluent or process streams are presented in Figure 7. By this evaluation procedure there are potentially harmful health and ecological effects for all total discharge severity (TDS) and total weighted discharge severity (WDS) values above 1. Each of the five streams exhibited potentially harmful health and ecological effects. The SAM/1A approach indicated that potential health and ecological effects were primarily due to organic compounds. However, the total DS for the streams (except gasifier ash and product gas vapors) include significant contributions from "worst case assump-

TABLE 1. OVERALL HEAT & MATERIAL BALANCE

	Mass Flow Rate kg/s	Mass Flow Rate (lb/hr)	Temperature °C	Temperature (°F)	Type of Heat	Enthalpy* kJ/kg	Enthalpy* (Btu/lb)	KW	Heat Flow Rate (1000 Btu/hr)	Percent
Inputs										
Coal	1.045	(8,292)			Potential	16,205	(6,967)	16,932	(57,700)	96.0
			-2	(29)	Sensible	-33	(-14)	-34	(-116)	-0.2
Net Stream	0.274	(2,174)	164	(328)	Sensible	2,847	(1,224)	780	(2,661)	4.4
Air	1.554	(12,334)	-2	(29)	Sensible	-28	(-12)	-43	(-148)	-0.2
Total	2.837	(22,800)						17,635	(60,167)	100.0
Outputs										
Dry Gas	2.299	(18,245)			Potential	6,020	(2,588)	13,840	(47,218)	78.5
			270	(518)	Sensible	265	(114)	609	(2,080)	3.5
Moisture	0.440	(3,492)	270	(518)	Sensible	2,910	(1,251)	1,280	(4,368)	7.3
Tars and Oils					Potential	26,193	(11,261)	566	(1,926)	3.2
	0.0215	(171)	270	(518)	Sensible	205	(88)	4	(15)	---
					Potential	20,139	(8,658)	86	(294)	0.5
Cyclone Dust	0.0043	(34)	270	(518)	Sensible	205	(88)	1	(3)	---
					Potential	8,806	(3,786)	952	(3,248)	5.4
Ash	0.108	(858)	93	(200)	Sensible	58	(25)	6	(21)	---
Heat to Cooling Water								128	(437)	0.7
Unaccounted for Losses								163	(557)	0.9
TOTAL	2.873	(22,800)						17,635	(60,167)	100.0

* Enthalpy is 25°C (77°F) and H_2O liquid. Potential heats are based on higher heating value (HHV).

TABLE 2. POTENTIAL ENERGY FLOWS BY LOWER HEATING VALUE

	Mass Flow Rate kg/s	LHV kJ/kg	LHV Heat Flow Rate kJ/s
Lignite Feed	1.045	14,783	15,448
Dry Gas	2.299	5,636	12,957
Tars and Oils	0.0215	24,398	525
Cyclone Dust	0.0043	19,821	85
Ash	0.108	8,706	940

TABLE 3. MAJOR GAS COMPONENTS

	Time	Volume Percent on Dry Basis					
	Hrs	CO	CO_2	H_2	O_2	N_2	CH_4
Dec. 13	1000	NA	NA	NA	NA	NA	NA
	1100	NA	NA	NA	NA	NA	NA
	1200	NA	NA	NA	NA	NA	NA
	1300	NA	NA	NA	NA	NA	NA
	1400	26.9	7.0	16.6	1.1	46.8	NA
	1500	24.1	8.6	16.6	1.1	48.2	0.6
	1600	26.1	7.2	16.5	1.0	47.3	1.0
	1700	28.0	6.8	16.7	1.2	45.8	0.7
	1800	27.1	6.6	16.7	1.1	46.5	1.2
	1900	27.4	6.7	26.9	1.2	46.4	0.7
	2000	24.6	8.3	16.5	1.1	47.6	1.0
	2100	25.3	8.0	16.5	1.1	47.5	0.7
	2200	27.3	7.1	16.8	1.0	45.7	1.2
	2300	27.4	7.2	16.9	1.0	45.6	1.1
Dec. 14	2400	27.6	7.1	16.6	1.1	45.3	1.4
	0100	26.6	7.7	16.0	0.9	46.6	1.4
	0200	27.0	7.1	17.1	1.0	45.6	1.3
	0300	27.7	6.4	18.0	1.1	44.5	1.5
	0400	28.2	6.2	17.4	1.2	44.8	1.5
	0500	28.9	6.3	17.3	1.2	44.7	0.9
	0600	25.7	7.7	18.3	1.3	45.4	0.9
	0700	28.8	6.3	18.7	1.3	43.3	0.9
	0800	29.2	5.9	19.0	1.1	43.2	NA
	0900	28.9	5.3	17.3	1.0	45.9	NA
	1000	26.4	8.9	17.2	1.2	44.8	NA

Notes: * Compositions are Radian process gas chromatograph readings normalized to 100 percent.

** Argon was not measured and is assumed to be 0.54 volume percent for all periods.

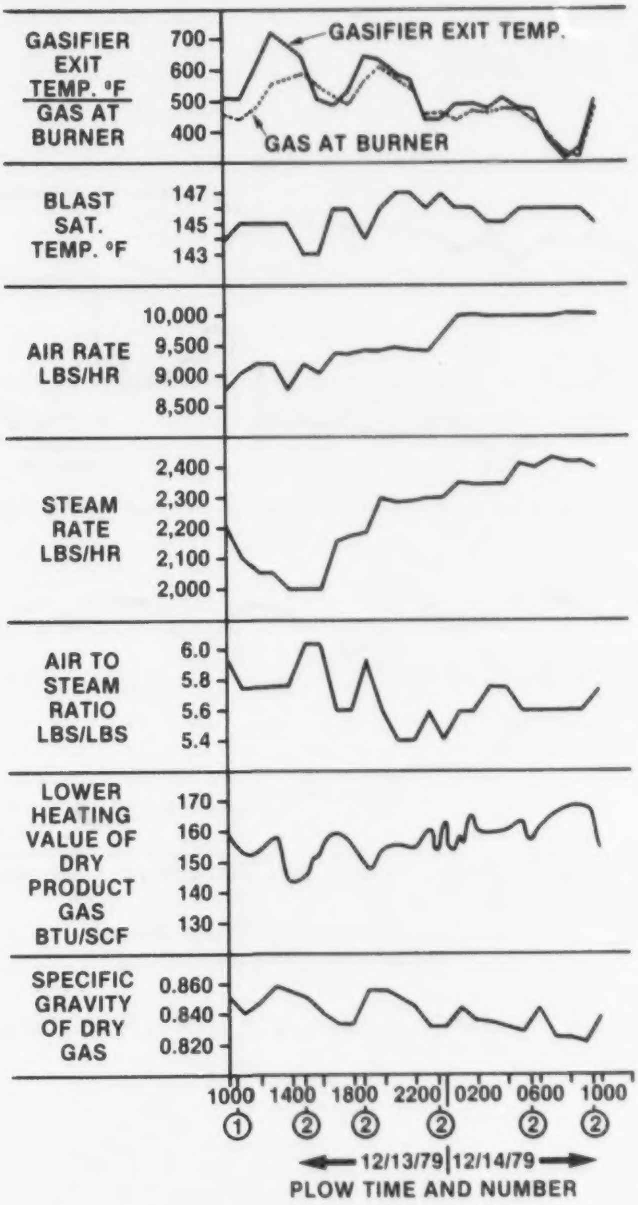

Figure 5. Process Variable for 24 Hour Period

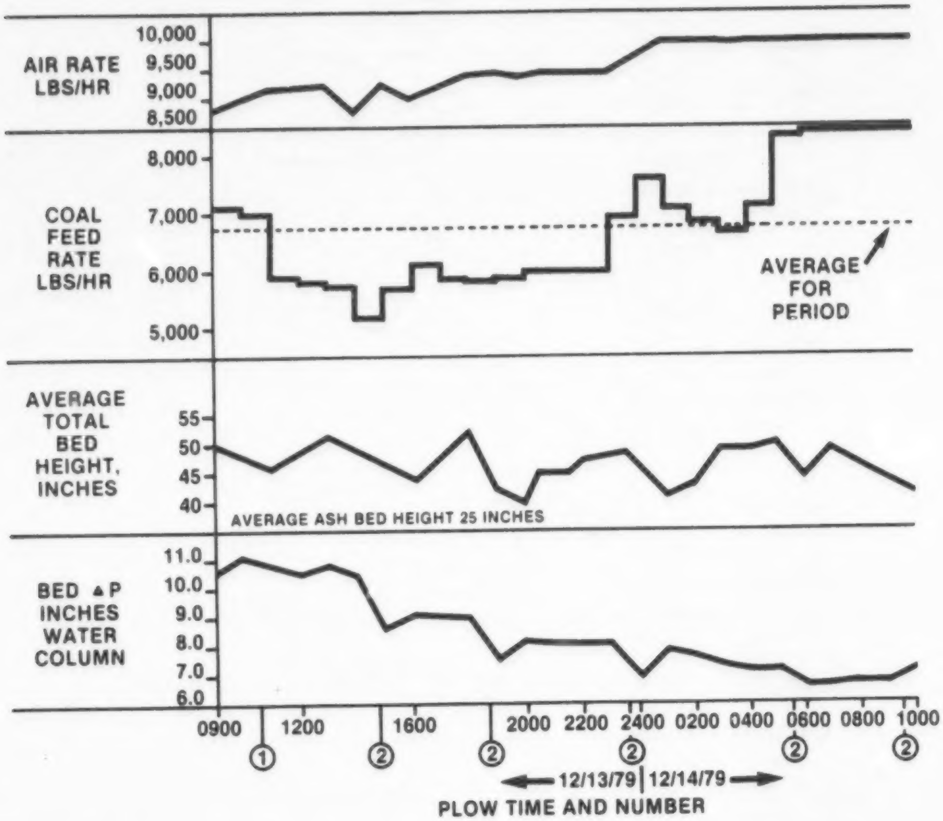

Figure 6. Bed Related Process Variable Plots for 25 Hour Lignite Run

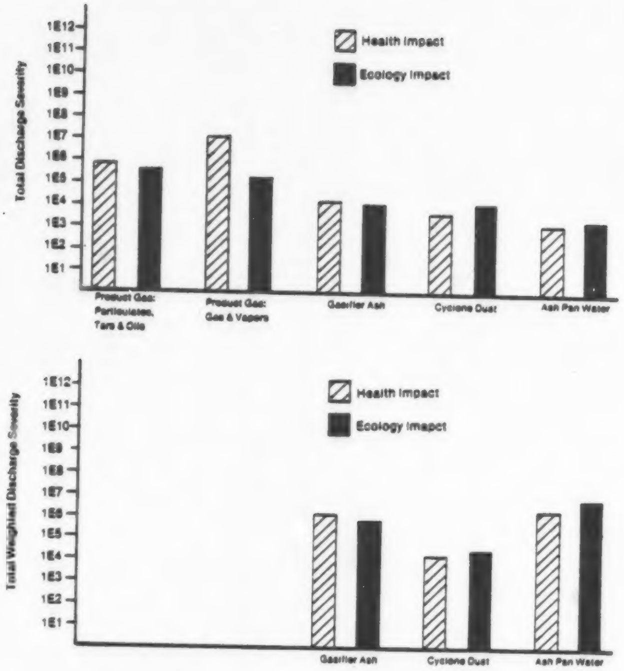

Figure 7. Total Discharge Severities and Weighted Discharge Severities of Effluent Streams

TABLE 4. SELECTED CHEMICAL ANALYSES

	Feed Coal (as received)%	Cyclone Dust WT.%	Tar WT.%
Moisture	34.10	0.59	--
Ash	7.54	38.21	0.20
Carbon	41.82	54.48	59.57
Hydrogen	2.83	1.48	8.40
Oxygen	12.70	2.82	30.75
Nitrogen	0.70	0.83	0.69
Sulfur	0.31	1.59	0.33
V.M.	30.68	--	--
F.C.	27.68	—	--
HHV, Btu/lb	6,967		
HHV, kJ/kg	16,205	8,607	11,261
LHV, kJ/kg	14,669	20,020	26,193

TABLE 5. CONTRIBUTIONS TO TOTAL DS AND TOTAL WDS BY WORST CASE ASSUMPTIONS GC/HECD DATA, AND EXPERIMENTALLY DETERMINED RESULTS

EFFLUENT STREAMS	Health				Ecology			
	WCA*	GC/HECD	EXP.	ORG./INORG.	WCA*	GC/HECD	EXP.	ORG./INORG.
Product Gas: Particulates, Tars and Oils	~97%		~3%	99.9%/0.1%	~99%		1%	99.7%/0.3%
Product Gas: Gas and Vapors	~100%	<1%	<1%	100%/0%	<1%		~100%	100%/0%
Gasifier Ash	~1%	~2%	~97%	18%/82%	<1%	~4%	~95%	5%/95%
Cyclone Dust	~83%		~17%	83%/17%	~23%		~77%	23%/77%
Ash Pan Water	~74%	~5%	~21%	99.9%/0.1%	~76%	~3%	~21%	79%/21%

*Worst Case Assumptions

tions" for the organics, which should be greatly reduced by more extensive analysis for specific organics (Table 5).

Inorganic elements, on the other hand, had the most significant contribution to the health and ecological impacts of the gasifier ash stream, with iron having the most significant health impact and phosphorus the most significant ecological impact. Inorganic elements did not contribute significantly to total DS or WDS for product gas or ash pan water health effects. However, phosphorus did make a significant contribution to the ecological effects of the ash pan water.

The findings in this source test evaluation indicate that the potential health and ecological effects of the ash pan water are significant. Even though the organic loading of the ash pan water was very low, the health and ecological DS and WDS of the stream were the result primarily of organics, other than the contribution of phosphorus to ecological impact. During the test program, ash pan water was continuously purged. Therefore, the concentrations of many parameters of concern in the stream were possibly held below anticipated levels of design operation using recycle, thereby reducing the total DS. However, continuous purging of the ash pan water provided a flow rate higher than design operation flow rate for the ash pan water and thereby raised the total WDS values to a level representative of commercial operation of the gasifier (Table 6).

Since organics provide the most significant contribution to the total DS of the product gas, these values would be reduced for the product gas combustion effluent due to the vast reduction in organic content following combustion. It should be noted that the SAM/1A approach treated the product gas as an effluent stream, which it is not, other than as a fugitive emission.

The SAM/1A results for gasifier ash and cyclone dust also showed potentially harmful health and ecological effects. On the other hand, bioassay tests conducted on the solid gasifier ash and cyclone dust indicated little or no health hazard. A neutral leaching of the two solid streams provided a liquid for bio-assay testing that showed a high level of ecological hazard. However, subjecting the gasifier ash and cyclone dust to (RCRA) leaching procedures (Reference 5) resulting in the solids being classified as non-hazardous (Tables 7, 8).

EMISSIONS FOLLOWING COMBUSTION

Presently, the main concern about the utilization of coal and coal-derived fuels in industry centers above emissions of oxides of sulfur, oxides of nitrogen, and particulates. While the actual emissions of SO_2 and NO_x due to low Btu gas combustion are dependent on application, the Riley test provided some indication of what the expected levels of these emissions might be.

During the two week test period, product gas from the gasifier was passed through a single stage cyclone for clean-up and transported directly to the large kiln burner. Because the temperature of the gas was maintained very close to that observed at the gasifier exit, not one gallon of product

TABLE 6. COMPARISON OF LIQUID STREAMS TO DRINKING WATER STANDARDS*

	NIPDWS*** µg/1	NSDWR**** µg/1	ASH PAN WATER** RANGE µg/1	ASH PAN WATER** AVERAGE µg/1	ASH PAN CARRY-OVER WATER µg/1	SERVICE WATER µg/1
As	50		11 - 30+	21+	9+	<10
Ba	1,000		91 - 230	170	250	100
Cd	10			<1	≤10	<10
Cl-		250,000	48,000-110,000	78,000	2,000	300
Cr	50			<1	<1	≤30
Cu		1,000	3 - 10	6	<1	70
F-	1,800		300 - 710	530	~1,000	~20
Fe		300	540 - 3,400	1,900	910	3,000
Pb	50		<1 - 2	<1.3	300	<10
Mn		50	27 - 96	58	11	40
Hg	2			<0.5+	<0.5+	
Se	10		<5 - 10+	<7	<5+	<10
Ag	50		2 - 30	14	20	<10
Zn		5,000	<3 - 12	<5.3	<3	80
NO_3^- (as N)		10,000		<20		
$SO_4^=$ (mg/1)		250	540 - 1,870	1,260		6.1
pH		6.5-8.5	10.2 - 11.3	10.8	5.0	4.3
TDS (mg/1)		500	1,250 - 2,050	2,250		52

*ICPES analytical results unless noted otherwise. Analysis performed by SSMS.
**Samples RM-18, RM-23, RM-49
***National Interim Primary Drinking Water Standards (Federal Register, 8/27/80).
****National Secondary Drinking Water Regulations (Federal Register, 7/19/79).
+Analysis performed by AAS.

TABLE 7. BIOASSAY TEST MATRIX

	Ames* (Health)	CHO** (Health)	RAM*** (Health)	RAT**** (Health)	Fresh-water Alga***** (Ecology)
Cyclone Dust	Negative	Low Toxicity	No Detectible Toxicity		
Gasifier Ash	Negative	No Detectable Toxicity	Low Toxicity		
Gasifier Ash Neutral Leachate	Negative	Low Toxicity		Not Toxic	Toxic
Cyclone Dust Neutral Leachate	Negative	No Detectable Toxicity		Not Toxic	Toxic

*Salmonella Mutagenesis Assay (Ames)
**Chinese Hamster Ovary Clonal Toxicity Assay (In Vitro Cytotoxicity Assay)
***Rabbit Alveolar Macrophage Assay (In Vitro Cytotoxicity Assay)
****Rodent Acute Toxicity (Acute in Vivo Toxicological Test)
*****Freshwater Alga (Selenastrum capricornutum) Toxicity Assay

TABLE 8. COMPARISON OF SOLID EFFLUENT EXTRACTS AND RCRA EXTRACT LIMITS

	RCRA Extract Limits* (5/19/80)	Gasifier Ash Leachate*	Cyclone Dust Leachate*
As	5,000	33	4
Ba	100,000	680	390
Cd	1,000	<0.5	<0.5
Cr	5,000	<1	<1
Pb	5,000	<2	<2
Hg	200	<0.5	<0.5
Se	1,000	6	2
Ag	5,000	<0.5	<0.5
Endrin	20	<2.0	<2.0
Lindane	400	<0.2	<0.2
Methoxychlor	10,000	<2.0	<2.0
Toxaphene	500	<100	<100
2,4-D	10,000	<0.8	<0.8
2,4,5-TP Silvex	1,000	<0.3	<0.3

*Concentrations in μg/liter.

gas tars and oils was condensed from the gas, nor was any significant amount of water-based condensate produced. With the exception of a light coating of dust which formed on the inside of the gas main, all product gas effluents leaving the gasifier cyclone outlet proceeded to the gas burner for combustion.

Combustion of the product gases was achieved in a low pressure baffle burner operating with combustion in the primary air zone at 33% of theoretical air and 213% of theoretical air overall. The theoretical adiabatic flame temperature for this mixture was 1077 C (1970 F). The flame produced was a long diffusion flame, ranging from 1.2 to 2 meters (4-7 feet) in diameter and 9 to 12 meters (30-40 feet) in length. Figure 8 illustrates several temperature profiles measured in the flame using a suction pyrometer.

No measurements of actual stack emissions were made. However, by analyzing the composition of the product gas being fed to the combustor, it was possible to make the following correlations.

The North Dakota (Indian Head) lignite gasifier feedstock for the 24 hour test period had an average sulfur concentration of $0.44g/10^6J$ (1.02 lb $S/10^6$ Btu). Some 53% of the sulfur being fed to the gasifier was being converted to reduced sulfur species in the product gas, with the majority of the remainder being retained by the gasifier ash stream. If 100% of the reduced sulfur species in the product gas were converted to sulfur dioxide during combustion, the resulting SO_2 emission level would be $0.49g/10^6J$ (1.10 lb $SO_2/10^6$ Btu) based on the heat value of the lignite feed. The New Source Performance Standards emission limit for SO_2 is $0.52g/10^6J$ (1.20 lb $SO_2/10^6$ Btu) for coal-fired boilers (Reference 6, Subpart D: Fossil Fuel Fired Steam Generators).

The average ammonia content of the product gas was 7.8×10^5 $\mu g/Nm^3$ and the average HCN concentration was 1.8×10^5 $\mu g/Nm^3$. About 26% of the nitrogen in the lignite feedstock was converted to reduced nitrogen species. Assuming that 100% of the reduced nitrogen species in the product gas was converted to NO_x during combustion, the resulting NO_x emission (as NO_2) would be 0.36g $NO_2/10^6J$ (0.841b $NO_2/10^6$ Btu) based on the heat value of the lignite feedstock. The NSPS emission level (Subpart D) for NO_x is 0.26g $NO_2/10^6J$ (0.60 lb $NO_2/10^6$ Btu) for coal fired boilers. While estimated NO_x emissions may be biased high, assuming 100% conversion of reduced nitrogen species to NO_x, it does not provide for the additional NO_x created due to thermal reaction of nitrogen and oxygen during combustion, which for many applications may be a significant contribution. For the specific test described here, the low combustion temperatures observed would likely minimize thermal production of NO_x, but high excess air levels would likely favor conversion of reduced nitrogen species to NO_x.

The particulate loading of the product gas stream was 4.76×10^5 $\mu g/Nm^3$ downstream of the cyclone. Particulate was assumed to be of the same composition as the cyclone dust, and the cyclone dust ash content was used for calculations to determine the particulate emissions after combustion. Basing the adjusted particulate loading upon the heat value of the lignite feedstock, the particulate emission after combustion would be 0.026g particulate/

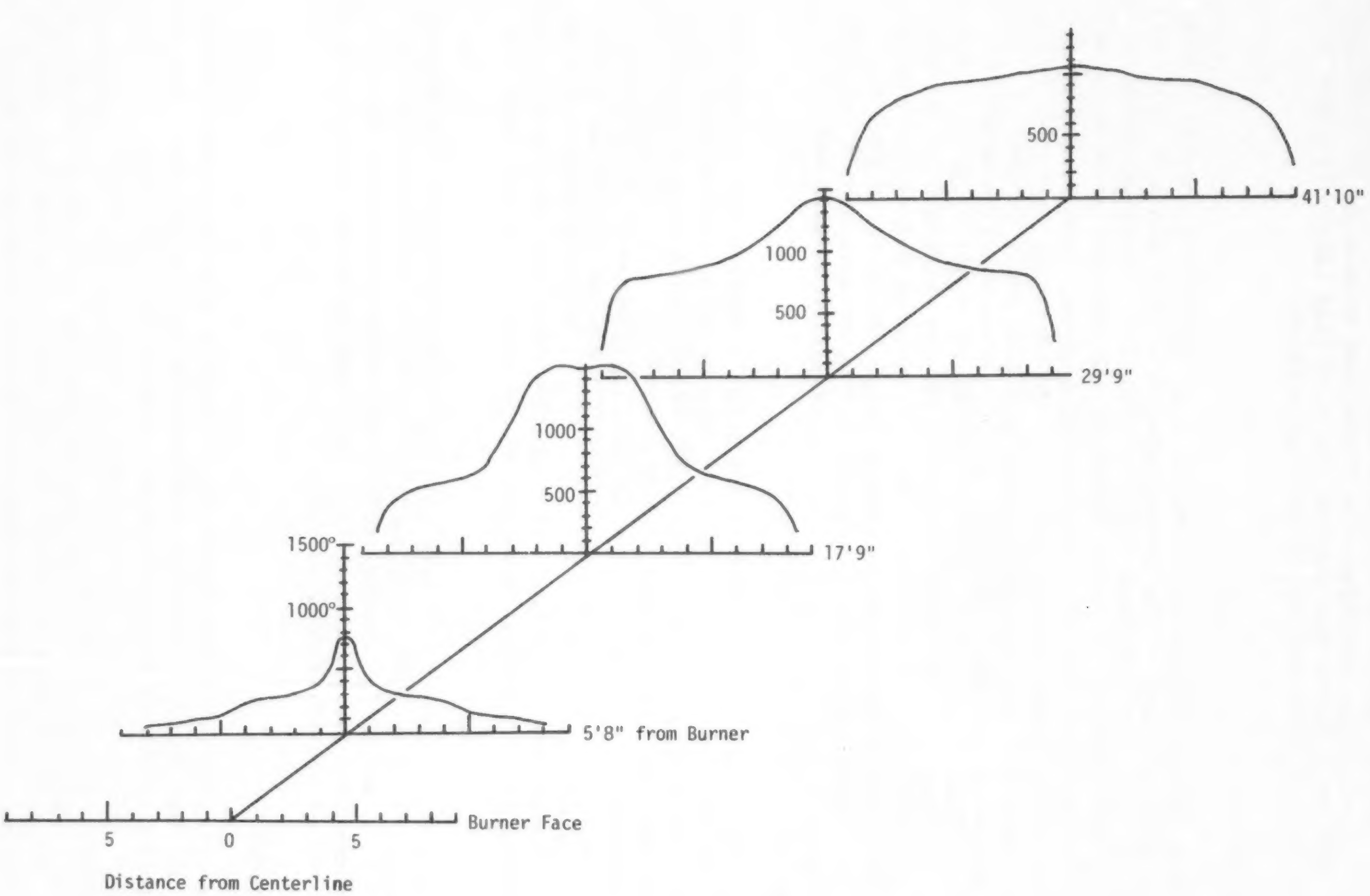

Figure 8. Low Btu Gas Flame Temperature Profile (9300 lb/hr rate)

10^6J (0.06 lb particulate/10^6 Btu). This particulate emission estimate does not consider particulate resulting from incomplete combustion of tars and oils. The NSPS (Subpart D) for particulate is 0.043g particulate/10^6J (0.10 lb particulate/10^6 Btu) for coal-fired boilers.

FUGITIVE EMISSIONS

The North Dakota lignite gasification test provided an opportunity for testing the effectiveness of the unique Riley coal feed and poke hole designs for minimizing fugitive emissions from the gasifier. Fugitive emissions of hydrocarbons were measured in the vicinity of the gasifier by several methods. Hydrocarbon concentrations, reported as methane, were less than on part per million as summarized in Table 9. Hydrocarbons were also measured in the off-gases from the nitrogen-pressurized coal bin. Concentrations here were 5-6ppm as methane. Readings of two carbon monoxide monitors maintained by Riley Stoker were recorded during the sampling period, and are summarized in Table 10. The maximum recorded CO concentration was 24 ppm with readings generally below this value. The Occupational Safety and Health Administration (OSHA) permissable exposure limit for CO is 50 ppm (see Reference 7). There is no OSHA regulation for hydrocarbons as a compound class. Propane is the lightest hydrocarbon regulated by OSHA and has a permissable exposure limit of 1,000 ppm.

Radian Corporation has performed STE's for a Chapman low Btu gasifier with a bituminous coal feedstock and a Wellman Galusha gasifier with an anthracite coal feedstock. The Chapman STE Report (Reference 8) presents coal feeder vent gas hydrocarbons concentrations of 2.5×10^6 µg/Nm^3. Similar measurements at the Wellman Galusha facility (Reference 9) resulted in coal hopper gas hydrocarbon concentrations of 1.4×10^6 µg/Nm^3 as methane. Related values measured at the Riley gas producer are many orders of magnitude less. These data demonstrate the relative reduction of fugitive emissions achieved by the controls employed on the coal bin at the Riley gas producer.

A sample was taken of the poke hole gas discharge during a simulated poking operation on the gasifier, to determine the effectiveness of the Riley poke hole design in keeping product gas sealed within the gasifier. Table 11 summarizes the results of that test, and shows the high degree of effectiveness of the Riley poke hole.

TRACE ELEMENTS

Trace elements enter the gasification process with the lignite feedstock and are subjected to the high temperatures of the process. Many elements, especially the more volatile ones, undergo volatilization in the hot areas of the system, and may either remain a vapor in the product gas, condense homogeneously, or condenses upon aerosol particles. Other elements are chemically transformed into gaseous species and are emitted in the product gas. Most trace elements remain in the coal solids and are emitted in the gasifier ash. Even though the majority of most elements are emitted with the solid effluent streams, RCRA extraction procedures analyses result in the classification of these solids as non-hazardous.

TABLE 9. ORGANIC VAPORS ANALYSIS

DATE	TIME	LOCATION	CONCENTRATION (ppm as CH_4)
12/13	1100 hrs	Gasifier Building --all walkways	1.5 ppm
12/13	2200 hrs	Gasifier Building --all walkways	1 ppm
12/13	2200 hrs	Gasifier Building --top of gasifier during poking operation	1 ppm
12/13	2223 hrs	Coal Bin --2-inch gate on top	5-6 ppm

TABLE 10. CARBON MONOXIDE MONITOR READINGS

Date	Time	Monitor 1*	Monitor 2**
12/13	1100		20 ppm
12/13	1500	1 ppm	
	1502		12 ppm
	1506		15 ppm
	1750	1 ppm	24 ppm
	1808		1 ppm
	2213		<0 ppm
12/14	0035		<0 ppm
	0235	1 ppm	<0 ppm

*Located in gasifier building on ground level, west wall.

**Located in gasifier building on gasifier poke hole level, north wall.

TABLE 11. POKE HOLE DISCHARGE DURING SIMULATED POKING OPERATION

DATE: 12/14

TIME: 0645 hours

FLOWRATE: 0.022 m^3/sec (actual)

GAS ANALYSIS:

N_2	95.4%
H_2	1.1%
O_2	0.2%
CO	Below detection limit
CH_4	Below detection limit
CO_2	Below detection limit

Minor and trace elements can be grouped according to the mechanism by which each is emitted. The elements primarily in the product gas can be considered highly volatile or transformed into gaseous compounds. Moderately volatile elements are predominately in the cyclone dust or product gas particulate and can be evaluated on the basis of volatilization and recondensation. Elements emitted predominately in the gasifier ash can be considered to be non-volatile elements.

For this source test evaluation, an element was considered to be highly volatile if 25% or more of its total mass was found in the gas and vapors portion of the product gas. These highly volatile elements were: bromine, cesium, chlorine, fluorine, gallium, iodine, selenium, silicon, sulfur and tellurium. An element was classified as moderately volatile if 25% or more of its total mass was found in the cyclone dust and particulates, tars and oils portion of the gas. These elements were: antimony, arsenic, chromium, germanium, lead, tin, and zinc.

The following elements were possible volatile and will acquire additional data to characterize their behavior definitively: beryllium, bismuth, cadmium, dysprosium, erbium, europium, gold, holmium, iridium, neodymium, osmium, palladium, platinum, praseodymium, radium, rhodium, ruthenium, silver, tantalum, terbium, thallium, thulium, uranium and ytterbium.

Figures 9 and 10 graphically present the elemental distribution in the effluent streams. The elements are listed in the order of increasing boiling points. In general, as the elemental boiling points increase, the predominance of elemental distribution shifts from the product gas to the gasifier ash. Although a general trend is evident, there is no direct correlation between elemental boiling point and distribution. The distribution of individual elements in the system is dependent not only on elemental boiling point, but also on much more complex properties, including chemical reactions within the gasifier, the volatility of compounds containing the elements, and solubility of compounds in the tars and oils.

Most of the elements classified as highly volatile from their distribution in the effluent streams were depleted in both the gasifier ash and cyclone dust. Cesium and gallium were exceptions and were enriched in both solids. This behavior is more characteristic of non-volatile elements.

Those elements considered to be moderately volatile from distributions fell into two major categories. Lead, chromium and zinc follwed the expected behavior of being depleted in the gasifier ash and enriched in the cyclone dust. Arsenic and antimony, however, were depleted in both solids. The distribution results show that both of these elements were found in the particulates, tars and oils fraction of the product gas. This indicates somewhat greater volatility than that of other moderately volatile elements. The behavior of germanium and tin was more characteristic of non-volatile elements, for germanium was enriched in both solids, and the enrichment ratios for tin were very close to the ash contents.

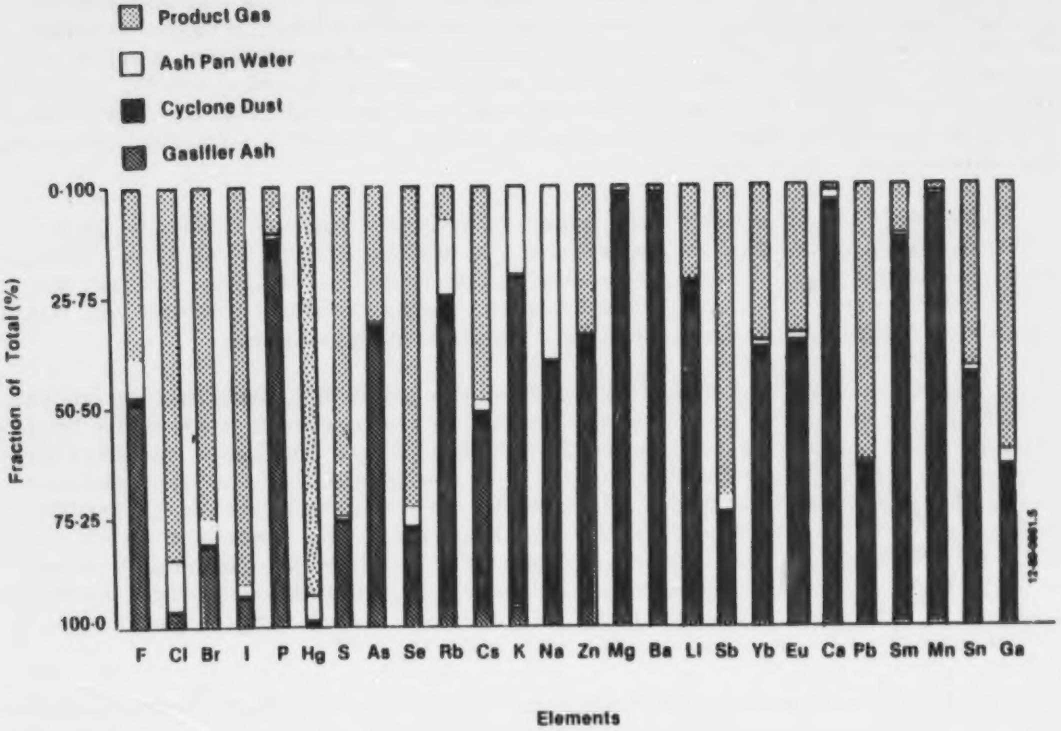

Figure 9. Stream Elemental Distributions as Percentage of Combined Effluent Streams Emission (Ordered by Increasing Elemental Boiling Points)

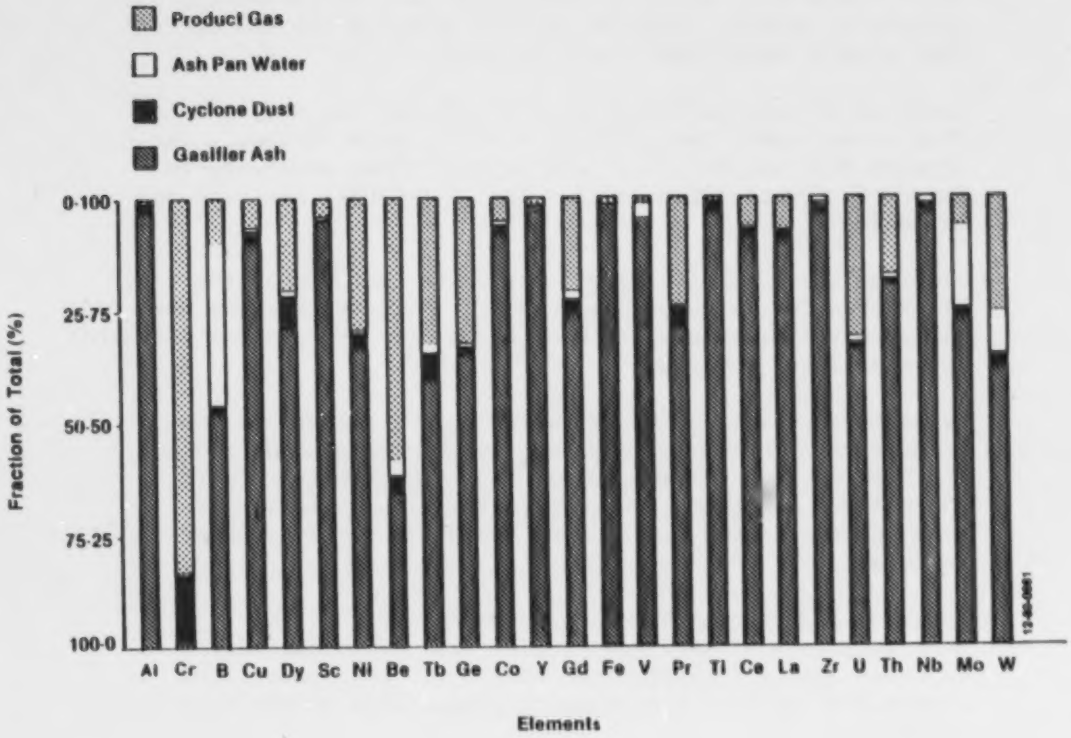

Figure 10. Stream Elemental Distributions as Percentage of Combined Effluent Streams Emission (Ordered by Increasing Elemental Boiling Points)

CONCLUSIONS

The major findings of this program are summarized below.

- Acute bio-assay tests of the gasifier ash and cyclone dust solids and neutral leachates of the gasifier ash and cyclone dust indicated no adverse health effects. Environmental bio-results of neutral leachates of the gasifier ash and cyclone dust showed significant toxic effects.

- Leaching studies conducted on the gasifier ash and cyclone dust to determine the effects of solid waste disposal, indicated that the materials are non-hazardous according to Resource, Conservation and Recovery Act (RCRA) protocol and standards.

- Although the gasification process emits over 50% of the lignite sulfur in the product gas, it will not require additional sulfur removal to meet New Source Performance Standards for coal fired boilers.

- Assuming that 100% of the ammonia and HCN present in the product gas are converted to NO_x during combustion, and not considering the contribution of thermally created NO_x in the boiler, additional NO_x controls will be necessary to meet the New Source Performance Standards for coal fired boilers.

- Additional particulate control measures will not be necessary to meet NSPS for particulate. This conclusion is based upon the particulate loading of the product gas downstream of the cyclone and the heat value of the lignite feedstock.

- Enclosed and pressurizing the coal bin, together with the nitrogen purge poke hole mechanism developed by Riley Stoker significantly reduce fugitive emissions.

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Session I: ENVIRONMENTAL SOURCE TEST AND EVALUATION RESULTS

Part B: Direct Liquefaction

Chairman: W. Gene Tucker
U.S. Environmental Protection Agency
Research Triangle Park, NC

Cochairman: Morris H. Altschuler
U.S. Environmental Protection Agency
Washington, DC

PB83-128249

ENVIRONMENTAL PROGRAM AND PLANS FOR THE EDS COAL LIQUEFACTION PROJECT

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ABSTRACT

The Exxon Donor Solvent (EDS) coal liquefaction project is a unique government/industry arrangement for developing EDS technology to the point that commercial plants can be designed with an acceptable level of risk. Project participants are the U.S. Department of Energy (DOE), Exxon Company, U.S.A., Electric Power Research Institute, Japan Coal Liquefaction Development Company, Inc., Phillips Coal Company, ARCO Coal Company, Ruhrkohle A.G., and AGIP S.p.A.

A broad environmental program is being advanced within the project to address plant emission, occupational health, and product-related environmental concerns associated with the direct liquefaction of coal. The current plans, status and outlook for the EDS Environmental Program are described to provide information on the overall strategy being followed for the acquisition of data relating to these concerns.

PROGRAM ORGANIZATION AND MANAGEMENT

The EDS Cooperative Agreement forms the basis upon which the government can participate in developing a technology in the national interest with industrial partners who develop and are the end users of the technology (1). Thus, the EDS Environmental Program Organization and Management reflects this arrangement in terms of the character and direction of the work activities.

Exxon Research and Engineering Company, the developer of the EDS process, has overall technical and execution responsibilities for the EDS project. Construction and operation support is provided by Exxon Company, U.S.A. The various contractual interfaces are shown in Figure 1.

Project direction is carried out by a number of committees consisting of members of sponsoring organizations participating in the cost sharing of the project as shown in Figure 2. The EDS Environmental Program draws upon the various elements of the Exxon organization for carrying out work activities related to their specific areas of expertise. The EDS Project Director has responsibility and authority for work direction, stewardship and communications.

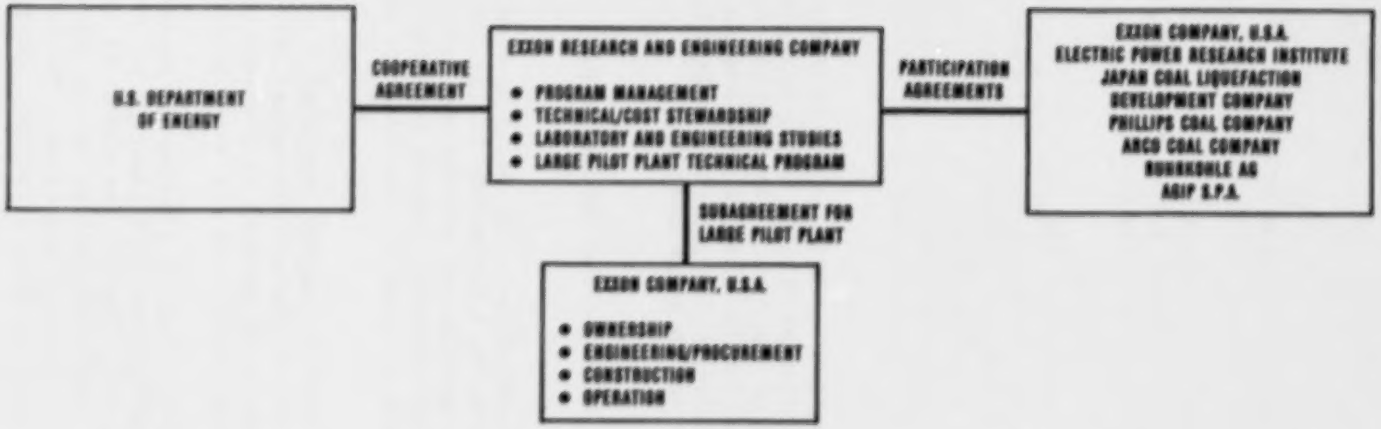
U.S. DEPARTMENT OF ENERGY
COOPERATIVE AGREEMENT
EXXON RESEARCH AND ENGINEERING COMPANY
• PROGRAM MANAGEMENT
• TECHNICAL/COST STEWARDSHIP
• LABORATORY AND ENGINEERING STUDIES
• LARGE PILOT PLANT TECHNICAL PROGRAM
PARTICIPATION AGREEMENTS
EXXON COMPANY, U.S.A.
ELECTRIC POWER RESEARCH INSTITUTE
JAPAN COAL LIQUEFACTION DEVELOPMENT COMPANY
PHILLIPS COAL COMPANY
ARCO COAL COMPANY
RUHRKOHLE AG
AGIP S.P.A.
SUBAGREEMENT FOR LARGE PILOT PLANT
EXXON COMPANY, U.S.A.
• OWNERSHIP
• ENGINEERING/PROCUREMENT
• CONSTRUCTION
• OPERATION

Figure 1. Contractual Interfaces EDS Coal Liquefaction Project

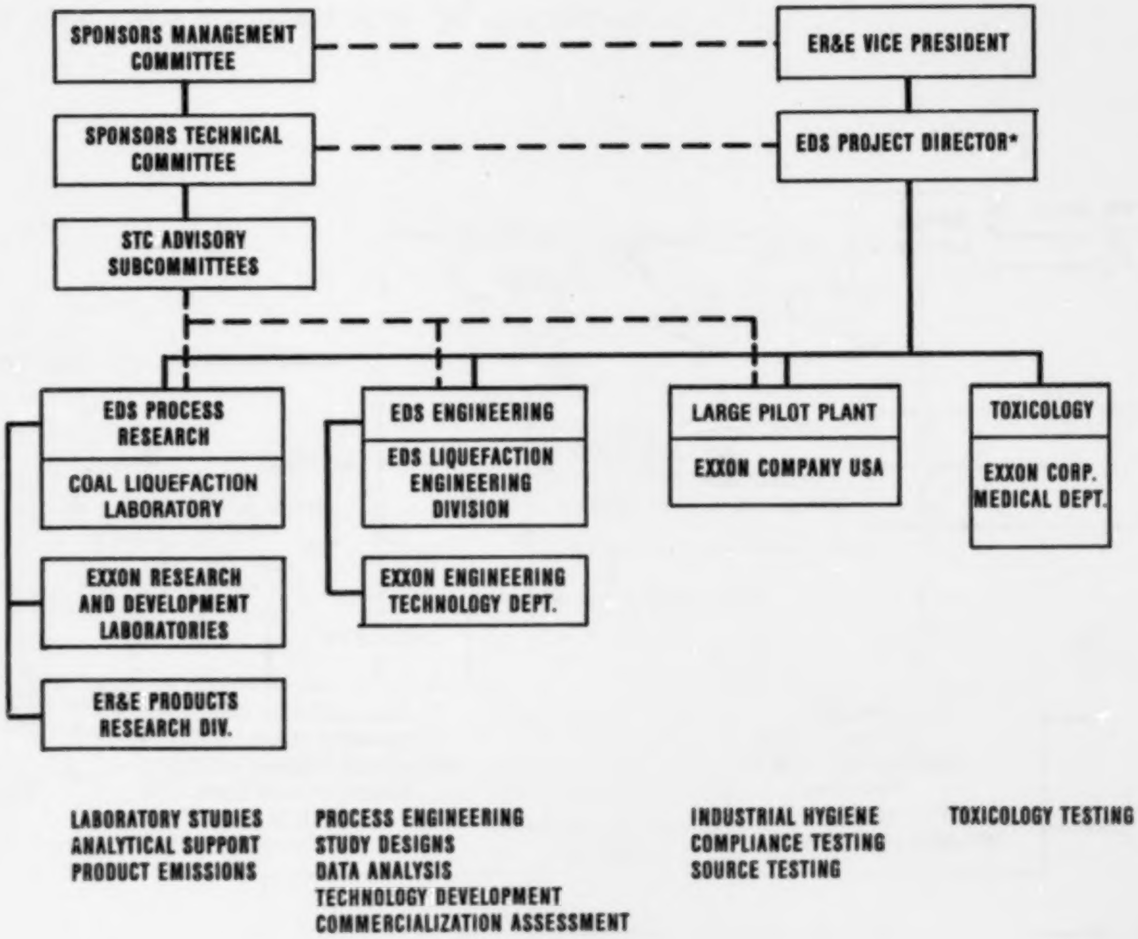
SPONSORS MANAGEMENT COMMITTEE
ER&E VICE PRESIDENT
SPONSORS TECHNICAL COMMITTEE
EDS PROJECT DIRECTOR*
STC ADVISORY SUBCOMMITTEES
EDS PROCESS RESEARCH
COAL LIQUEFACTION LABORATORY
EXXON RESEARCH AND DEVELOPMENT LABORATORIES
ER&E PRODUCTS RESEARCH DIV.
EDS ENGINEERING
EDS LIQUEFACTION ENGINEERING DIVISION
EXXON ENGINEERING TECHNOLOGY DEPT.
LARGE PILOT PLANT
EXXON COMPANY USA
TOXICOLOGY
EXXON CORP. MEDICAL DEPT.
LABORATORY STUDIES
ANALYTICAL SUPPORT
PRODUCT EMISSIONS
PROCESS ENGINEERING
STUDY DESIGNS
DATA ANALYSIS
TECHNOLOGY DEVELOPMENT
COMMERCIALIZATION ASSESSMENT
INDUSTRIAL HYGIENE
COMPLIANCE TESTING
SOURCE TESTING
TOXICOLOGY TESTING

Figure 2. EDS Coal Liquefaction Project Organization for EDS Environmental Program Activities

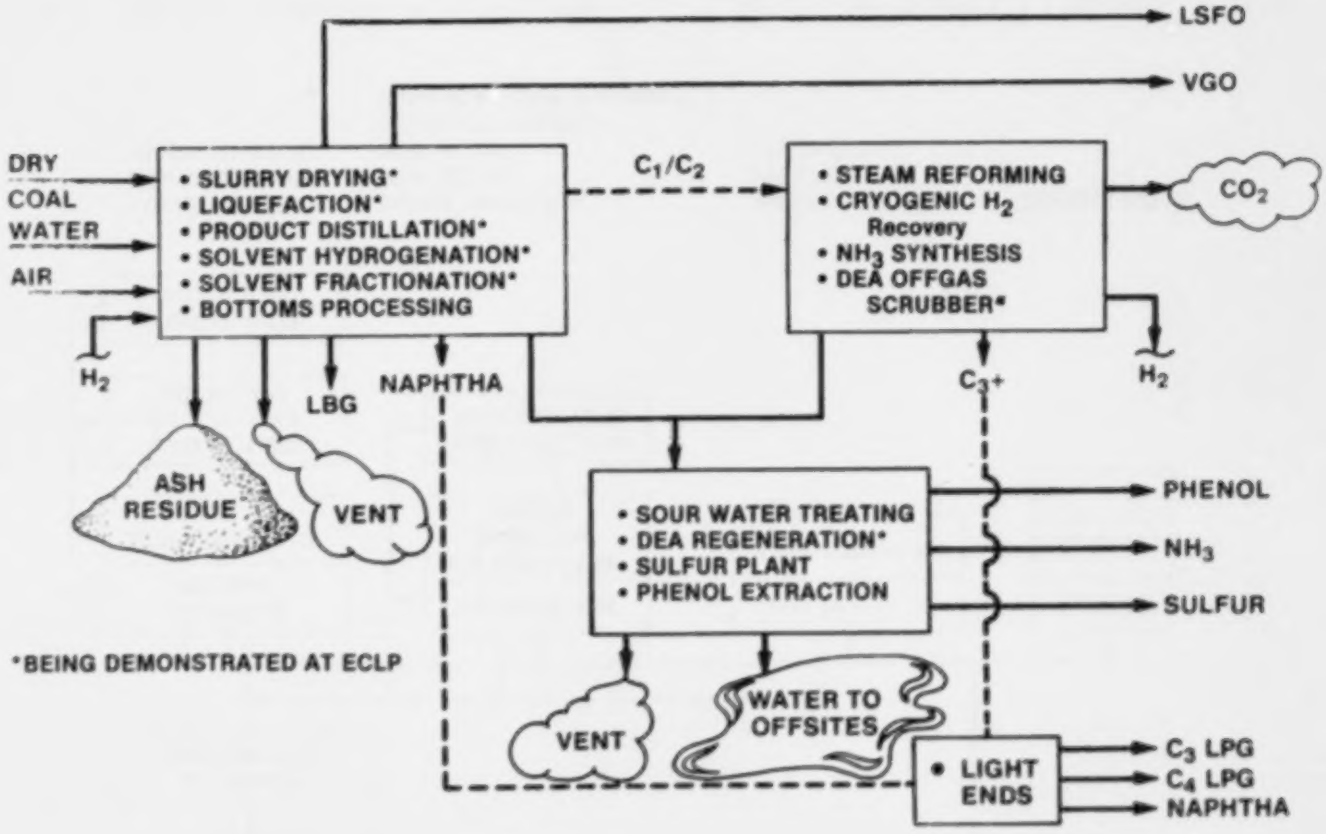
DRY
COAL
WATER
AIR
H_2
• SLURRY DRYING*
• LIQUEFACTION*
• PRODUCT DISTILLATION*
• SOLVENT HYDROGENATION*
• SOLVENT FRACTIONATION*
• BOTTOMS PROCESSING
LSFO
VGO
C_1/C_2
• STEAM REFORMING
• CRYOGENIC H_2 Recovery
• NH_3 SYNTHESIS
• DEA OFFGAS SCRUBBER*
CO_2
H_2
C_3+
ASH RESIDUE
VENT
LBG
NAPHTHA
• SOUR WATER TREATING
• DEA REGENERATION*
• SULFUR PLANT
• PHENOL EXTRACTION
PHENOL
NH_3
SULFUR
VENT
WATER TO OFFSITES
• LIGHT ENDS
C_3 LPG
C_4 LPG
NAPHTHA
*BEING DEMONSTRATED AT ECLP

Figure 3. EDS Commercial Plant Study Design Features

IMPLEMENTATION PLAN

The overall objective of the EDS Environmental Program is to assure a safe and environmentally sound process. Bench-scale research, small pilot unit operation, engineering design and technology studies, and operation of a 250 ton-per-day coal liquefaction pilot plant (ECLP) are collectively being utilized to provide an environmental data base to meet this overall objective. This effort is summarized in Table 1.

A conceptual design for a commercial scale plant operating on Illinois bituminous coal has been recently completed for a Western Illinois location (2). This engineering study depicting the state of EDS technology in 1978, after approximately ten years of development work, was carried out in sufficient detail to define environmental control needs and costs for siting a commercial plant. Studies of this type are used for research guidance in the environmental program. A similar study reflecting potential process improvements conceived after 1978, is currently underway for a conceptual plant operating on Wyoming coal in a Western U.S. location.

The large 250 ton-per-day pilot plant at Baytown, Texas plays an important role in providing representative commercial streams for environmental and health studies of EDS materials in the various stages of production from raw materials to products and effluents. Chemical and physical characterization of pilot plant materials in conjunction with bioassay and occupational exposure data from the pilot plant constitute the data base for making judgments on the potential environmental acceptability of the EDS process for commercialization.

Program emphasis is on the aspects of the EDS process which conceivably can be scaled to commercial size facilities. The basic EDS process streams, plant products and commercial plant design features are shown in Figure 3 along with those features undergoing demonstration at the large 250 ton-per-day pilot plant (ECLP).

In the EDS process, coal is dried and slurried with hydrogenated recycle solvent and reacted in a liquefaction reactor at approximately 800°F and 2000 psia. The three phase product stream from the liquefaction is separated by a combination of atmospheric and vacuum distillation. The liquid fuel products are naphtha, a middle distillate (LSFO) and a vacuum gas oil (VGO). If desired, the vacuum gas oil stream may be recycled to extinction in the liquefaction reactors to provide a product slate with a boiling range below 800°F. The basic environmental control units involve sulfur, phenol and ammonia recovery.

The major operating units at ECLP, as they pertain to the EDS process are the coal preparation section, the slurry drying section, the liquefaction section, the product recovery section and the solvent hydrogenation section. Other areas of ECLP are similar in nature to typical support units of any petroleum refinery and include DEA regeneration and gas treating, hydrogen compression, safety facilities, waste handling, sour water collection facilities, utilities and tankage.

TABLE 1. EDS ENVIRONMENTAL PROGRAM IMPLEMENTATION

- Carry out Conceptual Plant Design Studies
  - To Identify Areas Requiring Additional Research
  - To Develop Updated Investment Costs and Economics
  - To Provide Base Point for Initial Commercialization of a Future Pioneer Plant
- Carry out Pilot Plant Demonstrations
  - Stream Characterization and Source Testing
  - Monitor Workplace Exposures
  - Equipment Design and Scale-up Data
  - Representative EDS Products for Combustion Emission Testing
- Develop Integrated Environmental and Health Assessment Data Base
  - Chemical and Physical Properties
  - Bioassay and Occupational Exposure Data

Not included in the ECLP demonstration is processing of the vacuum bottoms material which consists largely of 1000°F+ liquids, unconverted coal and coal mineral matter. Work is in progress to evaluate the use of bottoms partial oxidation processing for hydrogen/fuel gas generation and direct combustion of bottoms for plant fuel. Conceptual Commerical Plant Study designs carried out to date have utilized FLEXICOKING for vacuum bottoms processing. FLEXICOKING, a commercial petroleum process that employs integrated coking and gasification reactions in circulating beds, recovers essentially all of the feed carbon from the bottoms material as product liquid or plant fuel gas. A small amount of carbon is purged from the unit with the coal mineral matter. Leachate tests have been performed on the solids from FLEXICOKING to identify any problems requiring resolution (3). Environmental assessments will need to be carried out for the other bottoms processing/ utilization options being developed for the EDS process.

PROGRAM HIGHLIGHTS

Conceptually the program consists of related environmental and health monitoring, testing, engineering studies and assessments. Specific activities within the EDS Environmental Program include monitoring and testing of process streams and occupational exposures as well as engineering and laboratory studies of environmental controls. The following summarizes the major activities in each of the environmental areas of air, water, solid wastes, human health, ecology and product utilization highlighted in Table 2.

AIR EMISSIONS

The air emissions activity consists of compliance monitoring associated with the large pilot plant (ECLP) operations at Baytown, Texas, design studies to define control technology options for criteria pollutants in conceptual commercial plants and in-plant testing to characterize noise and process emission sources. The focus of the pilot plant test program is to assess fugitive, particulate, and potentially toxic emissions during both normal and intermittent operations to provide a data base for environmental assessments for future plants and the design of emission control facilities where needed.

WASTEWATER TREATMENT

Treatment of all process and other water effluent streams from the ECLP operations is being carried out in the adjacent Baytown Refinery facilities as provided in the environmental permit for the pilot plant. An extensive in-plant test program is underway to monitor and characterize raw process water streams for variability, composition (including trace

TABLE 2. EDS ENVIRONMENTAL PROGRAM HIGHLIGHTS

- Air Emissions
  - Control Technology Options for Criteria Pollutants
  - In-plant Testing
  - Assessment of Fugitive H/C Emissions
- Wastewater Treatment
  - Characterization of Raw Process Streams
  - Treatability Studies
  - Bench Scale Testing
- Solid Waste Disposal
  - Physical and Chemical Properties
  - Solid Waste Management Techniques
- Occupational Health
  - Seven Phase Worker Protection Program
  - Workplace Monitoring
  - Medical Surveillance
- Toxicity
  - Acute, Subchronic, Chronic Testing
  - Environmental and Product Streams
  - Human and Ecological Systems
- Product Utilization
  - Raw EDS Products
  - Combustion Emissions

metals), and treatability. Offsite bench-scale treating tests will be carried out on samples from large pilot plants to establish the water treatment requirements for a commercial plant. This work will serve to confirm the basis for commercial plant design studies being conducted in parallel with the test program to define quantities and streams for a commercial plant. An independent inplant test program has been completed at ECLP by the U.S. Environmental Protection Agency (EPA) to serve as a data base for EPA's research activities in direct coal liquefaction.

SOLID WASTE DISPOSAL

Solid waste management techniques and requirements are being developed as part of a study design activity for a conceptual commercial plant. In addition, in-plant test work to characterize the solid wastes on all project coals will be carried out to determine handling and disposal properties.

OCCUPATIONAL HEALTH

A seven-phase program involving engineering controls, industrial hygiene, operations and laboratory work practices, personal hygiene, medical surveillance, and health education forms the basis for the ECLP Occupational Health Program (4). Specific goals are to assure a safe and healthy work environment at ECLP and to provide an expanded data base for future production facilities. The industrial hygiene data base being generated includes pre-startup and periodic baseline surveys, routine monitoring of process and mechanical personnel, and area monitoring of special operations such as maintenance. Over 1200 personal and area samples have been generated during the first of three program coals. An independent industrial hygiene in-plant survey has been carried out at ECLP by the National Institute of Occupational Health and Safety (NIOSH) to support NIOSH research in direct coal liquefaction.

TOXICITY

The goals of the Toxicity Program are to 1) identify toxic hazards to either human health or ecological systems, 2) assess the risks those hazards present, and 3) assess the commercial readiness of the EDS process technology in the light of those risks and hazards. The program provides for analytical characterization, and in-vitro and invivo testing of samples of EDS product, process and waste streams. The testing will encompass the following: acute oral, dermal and inhalation toxicity; eye and skin irritation; skin sensitization; mutagenicity; carcinogenicity; subchronic toxicity, teratology and reproductive effects; and fish and daphnia toxicity, daphnia and algae growth and inhibition.

PRODUCT UTILIZATION

Downstream processing/refining of EDS products and subsequent marketing and use of such upgraded products is outside the present scope of the EDS project. However, the middle distillate (LSFO) and vacuum gas oil (VGO) products can be used directly or as a blendstock for existing petroleum products. Combustion emission testing of EDS fuel oil blends has been initiated (5). In addition, all products will be evaluated for toxic hazards to human health and ecological systems recognizing the need for handling and transporting of EDS products from a production facility.

STATUS AND OUTLOOK

The environmental data base being generated within the EDS project is designed to complement programs being carried out in cooperation with government agencies. In this manner, the EDS process is expected to meet commercial environmental design requirements and resolve present concerns for the class of materials which exist in coal liquefaction plants.

The program status is highlighted in Table 3. To date, 3900 hours of operation on Illinois No. 6 coal have successfully been completed at the large EDS Pilot Plant in Baytown, Texas (6). All environmental data acquisition objectives for this run have been met and a major data analysis and laboratory investigation effort is underway. Present operating plans for the pilot plant call for operation on a subbituminous and a lignite coal with further environmental testing to establish a data base for three different types of coals.

The EDS process is still evolving with the introduction of bottoms recycle operations at ECLP in August, 1981, and the work in progress to evaluate various bottoms processing and utilization options. Environmental data acquisition efforts will be integrated into these process development areas consistent with the overall strategy of the EDS Environmental Program.

As presently funded, the EDS project will terminate June 30, 1982, with the subsequent dismantling of ECLP and completion of the EDS environmental work outlined in this paper. Under the terms of the EDS Cooperative Agreement, work of a non-proprietary nature is to be made available to the EDS Project Sponsors. The reporting system for the EDS Project consists of monthly, quarterly, and annual technical reports and assures that all technical contract data for the EDS Environmental Program will be in the public domain through DOE sponsorship of the project.

TABLE 3. EDS Environmental Program Status

- Illinois Coal Study Design and Pilot Plant Operations Complete
- Wyoming Coal Study Design and Pilot Plant Operations Underway
- EDS Process Still Evolving
  - Bottoms Processing Studies
  - Bottoms Recycle Under Demonstration at ECLP
  - Product Utilization Emphasis on Distillate Fuels
- Data Analysis and Laboratory Work will Continue for Three Types of Coals

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2. , "EDS Commercial Study Design Update, Illinois Coal," FE-2893-62, February, 1981.

3. Boyer, G. T. et al, "Water Pollution Control in the Exxon Donor Solvent Coal Liquefaction Process," AIChE 87th National Meeting, Boston, Mass., August 21, 1979.

4. Montgomery, C. Hunter, "Coal Liquefaction Occupational Health Program," 65th Annual Meeting of the American Occupational Medical Association, Detroit, Mich., April 21-25, 1980.

5. Ryan, D. F., Panzer, J., "PNA Emissions From Combustion of EDS Fuel Oils," 6th Annual EPRI Contractor's Conference on Coal Liquefaction, May 13-14, 1981.

6. Brackett, R. H., Clunie, T. J., Goldstein, A. M., "Exxon Donor Solvent Coal Liquefaction Process: Exxon Coal Liquefaction Plant Operations," 6th Annual EPRI Contractors' Conference on Coal Liquefaction, May 13-14, 1981.

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PB83-128256

SAMPLING AND ANALYSIS OF PROCESS AND† EFFLUENT STREAMS FROM THE EXXON DONOR SOLVENT COAL LIQUEFACTION PILOT PLANT

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Columbia, MD 21045

ABSTRACT

Under contract to the U.S. Environmental Protection Agency (EPA), Hittman Associates, Inc. performed a sampling and analysis of process discharge streams from the Exxon Donor Solvent (EDS) coal liquefaction plant in Baytown, Texas. Twenty-four streams were sampled and 2,200 samples were returned to Hittman's laboratory for analysis. The chemical analyses of these samples included water quality parameters, GC/MS, GC/FID, and bioassays. Analyses were also performed to determine the accuracy and precision of the data and to determine the variability of stream components due to process variations. Preliminary results are available and data evaluation for the Source Test and Evaluation Report is underway.

INTRODUCTION

The EPA Industrial Environmental Research Laboratory is developing a data base in support of EPA's synfuels program. This data base includes data obtained through sampling and analysis of environmentally significant waste and process streams from existing synfuels facilities. Environmental data acquired in this program will be used to assess the environmental impacts of synthetic fuels plants and evaulate the effectiveness of control technologies.

The Exxon Donor Solvent process is one of several processes used to convert coal to liquid fuel which is under investigation. In this process a "donor solvent" is first hydrogenated and then mixed with pulverized coal and hydrogen. Hydrogen is transferred from the donor to components of the coal, thereby liquefying the coal. Subsequent fractionation of the resulting mixture yields hydrocarbon products. The donor solvent is separated and recycled for hydrogenation. The EDS process is being studied at the Exxon Coal Liquefaction Pilot Plant (ECLP) in Baytown, Texas. Hittman Associates, Inc. performed sampling and analysis of the plant's process discharges. The results of the analysis will be used by EPA to assess the environmental impacts of the EDS process. It should be noted that although the pilot plant represents a commercial facility, there are significant differences. Three major differences are: (1) the pilot plant has no wastewater treatment facility; all sour water streams are combined and sent to the adjacent Baytown Refinery wastewater treatment plant; (2) acid gas (H_2S) removed from the gaseous streams also is treated by the refinery sulfur recovery system, while a commercial facility would have its own sulfur recovery system; and (3) the vacuum bottoms (carbonaceous residue) is drummed and stored at the pilot plant, whereas in a commercial facility this would be either treated in a Flexicoker® or gasified to produce hydrogen.

The criteria used to select the ECLP streams to be sampled are presented in detail in the EDS Test Plan. (Hittman Associates, Inc. Environmental Test Plan for the EDS Pilot Plant in Baytown, Texas. EPA Contract No. 68-02-3147, February 1981). The intent was to select streams which would be found in a commercial facility or would be similar to such streams and were significant either to potential environmental impacts or to control technology evaluation. No internal process streams were sampled. The selected streams are listed in Table 1. They include 15 sour water streams and the combined sour water that leaves the ECLP for treatment, naphtha, light solvent fuel oil, combination product, feed coal, vacuum bottoms, and several gaseous streams relevant to control technology evaluation. The sampling program consisted of three separate efforts: (1) collection of composite samples over a three-day period for each of the selected streams; (2) collection of a set of samples from six of the streams to determine process, sampling, and analytical variability; and (3) collection and on-site analysis of the gaseous samples on a one-time only basis. The primary liquid samples from the ECLP plant were split, composited, preserved, and returned to the Hittman Laboratory for analysis.

The analytical program was based on a combined Level 1/Level 2 methodology using a directed analytical approach. The combined methodology was adopted because in conducting consecutive Level 1/Level 2 analyses, the time interval between the two efforts allows for major changes in the facility, particularly in the case of pilot operations. A directed analytical approach was chosen because it permits complete analyses of a selected group of high-priority streams which guide the analyses of components of the priority streams. A complete discussion of the analytical program is presented in the EDS Test Plan. A paper devoted to the EDS analytical work is included in this symposium (Higman, et al. "Problems Associated with the Analysis of Synfuel Products, Process, and Waste Water Streams").

PROCESS DIAGRAM AND SAMPLE POINTS

The first step of the EDS process is coal preparation. Figure 1 shows the coal preparation area. Coal is transported to the plant via a bottom-dump rail car and taken to a 5,000-ton storage silo. The coal is then crushed and dried before entering the slurry drier tank.

The crushed coal is mixed with recycle solvent and fed to the slurry drier (Figure 2). The coal-solvent mixture is pumped, along with hydrogen, to the preheat furnace and then to the liquefaction reactors. These reactors are kept at 840°F and 1,900 to 2,000 psig. The off-gas from the

TABLE 1. ECLP SAMPLE POINTS

Aqueous Sample Points

Stream	Process Area
Sour Water - Recycle Gas Cold Separator Drum	Slurry Drying and Liquefaction
Rich DEA - Liquefaction DEA Scrubber	Slurry Drying and Liquefaction
Scrubber Water - Recycle Gas Water Scrubber	Slurry Drying and Liquefaction
Sour Water - Atmospheric Fractionator	Product Distillation
Cold Sour Water - Atmospheric Fractionator	Product Distillation
Sour Water - Steam Ejector Condensate Pump	Product Distillation
Scrubber Water - Water Scrubber Unit	Solvent Hydrogenation
Rich DEA - DEA Scrubber	Solvent Hydrogenation
Condensed Water - P-302 & P-304	Solvent Hydrogenation
Rich DEA - Hydrocarbon Skimming Drum	Fuel Gas Treating and DEA Regeneration
Lean DEA - DEA Regenerator	Fuel Gas Treating and DEA Regeneration
Sour Water - Fuel Gas DEA Scrubber Sour Water Pump	Fuel Gas Treating and DEA Regeneration
Scrubber Water - Acid Gas Water Scrubber	Fuel Gas Treating and DEA Regeneration

TABLE 1. (CONTINUED)

Solid Sample Points

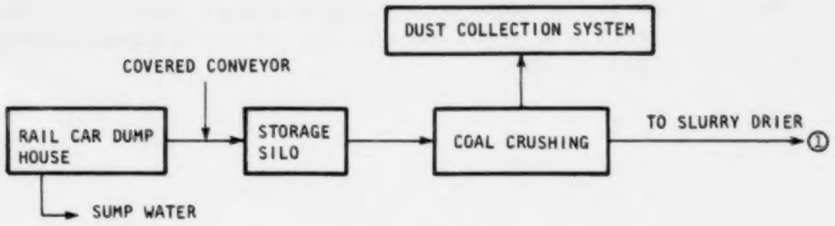
Stream	Process Area
Feed Coal	Coal Prep
Vacuum Bottoms	Product Distillation

Product Sample Points

Stream	Process Area
Naphtha	Solvent Hydrogenation
Light Solvent Fuel Oil	Solvent Hydrogenation
Combined Product	Solvent Hydrogenation

Gaseous Sample Points

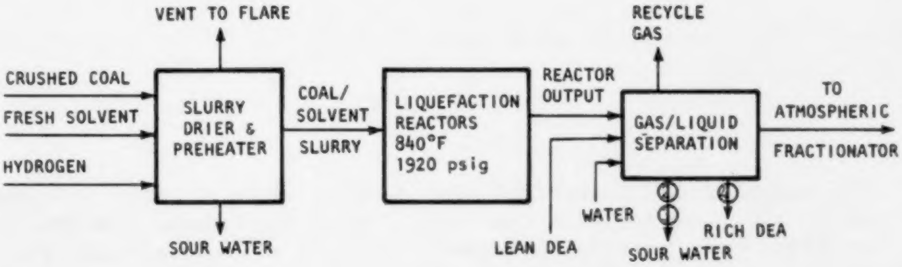
Stream	Process Area
Offgas - DEA Regenerator	Fuel Gas Treating and DEA Regeneration
Offgas - Fuel Gas Condensate Separator Drum	Fuel Gas Treating and DEA Regeneration
Acid Gas to Refinery	Fuel Gas Treating and DEA Regeneration
Offgas - Fuel Gas DEA Scrubber	Fuel Gas Treating and DEA Regeneration


DUST COLLECTION SYSTEM
COVERED CONVEYOR
RAIL CAR DUMP HOUSE
STORAGE SILO
COAL CRUSHING
TO SLURRY DRIER
①
SUMP WATER

1 - Feed Coal

Figure 1. Coal Preparation Area

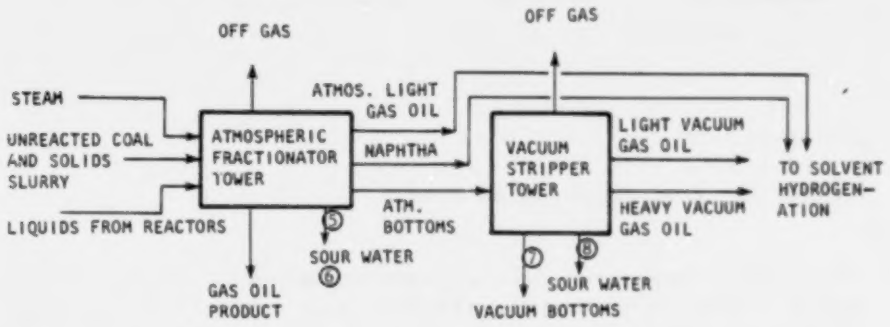
reactors is separated into a vapor stream and a slurry stream. The vapor stream is condensed, yielding sour water, hydrocarbons, and an off-gas stream. The sour water stream goes to the sour water disposal tank. The condensed hydrocarbons are mixed into the slurry stream and sent to the atmospheric fractionator. The off-gas from the separator drums is scrubbed with DEA and water and recycled back to the process.


VENT TO FLARE
CRUSHED COAL
FRESH SOLVENT
HYDROGEN
SLURRY DRIER & PREHEATER
SOUR WATER
COAL/ SOLVENT SLURRY
LIQUEFACTION REACTORS 840°F 1920 psig
REACTOR OUTPUT
RECYCLE GAS
GAS/LIQUID SEPARATION
TO ATMOSPHERIC FRACTIONATOR
WATER
LEAN DEA
②
③
④
SOUR WATER
RICH DEA

2 - Sour Water - Recycle Gas Cold Separator Drum
3 - Scrubber Water - Recycle Gas Water Scrubber
4 - Rich DEA - Liquefaction DEA Scrubber

Figure 2. Slurry Drying and Liquefaction Area

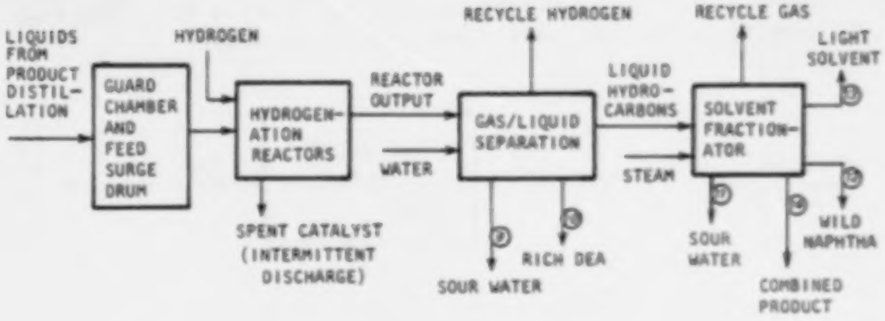
The slurry stream is fed to the atmospheric fractionator, where it is separated into atmospheric bottoms, naphtha, atmospheric light gas oil, and off-gas (Figure 3). The off-gas is condensed and separated into sour water, condensed hydrocarbons, and raw fuel gas. The atmospheric bottoms are fed to the vacuum fractionator, where the off-gas, light and heavy gas oil, and vacuum bottoms are separated. The products from the atmospheric and vacuum fractionators are combined and fed to the solvent hydrogenation section for further processing.


OFF GAS
OFF GAS
STEAM
ATMOS. LIGHT GAS OIL
UNREACTED COAL AND SOLIDS SLURRY
ATMOSPHERIC FRACTIONATOR TOWER
NAPHTHA
VACUUM STRIPPER TOWER
LIGHT VACUUM GAS OIL
TO SOLVENT HYDROGEN-ATION
LIQUIDS FROM REACTORS
⑤
ATM. BOTTOMS
HEAVY VACUUM GAS OIL
SOUR WATER
⑥
⑦
⑧
GAS OIL PRODUCT
SOUR WATER
VACUUM BOTTOMS

5 - Sour Water - Atmospheric Fractionator
6 - Cold Sour Water - Atmospheric Fractionator
7 - Vacuum Bottoms
8 - Sour Water - Steam Ejector Condensate Pump

Figure 3. Product Distillation Area

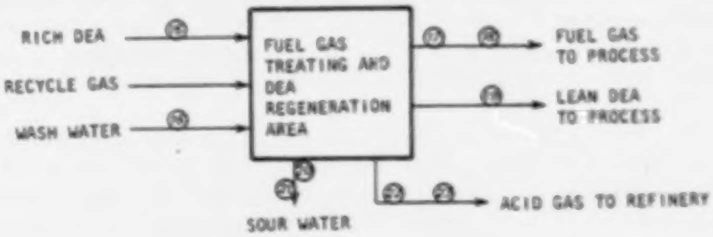
The output from the product distillation area is mixed with hydrogen and fed to the hydrogenation reactors (Figure 4). These reactors consist of four fixed-bed reactors containing a nickel-molybdate catalyst. The reactor output is separated into hydrogen-rich gas, sour water, and a hydrotreated liquid stream after passing through hot and cold separator drums. The hydrogen-rich gas is scrubbed with DEA and water and the hydrogen is recycled back to the process. The solvent fractionator separates the hydrotreated liquids into naphtha, light solvent fuel oil, gas oil product, fresh recycle solvent, and raw fuel gas.


LIQUIDS FROM PRODUCT DISTILLATION
GUARD CHAMBER AND FEED SURGE DRUM
HYDROGEN
HYDROGENATION REACTORS
SPENT CATALYST (INTERMITTENT DISCHARGE)
REACTOR OUTPUT
WATER
RECYCLE HYDROGEN
GAS/LIQUID SEPARATION
9
SOUR WATER
10
RICH DEA
LIQUID HYDROCARBONS
STEAM
RECYCLE GAS
SOLVENT FRACTIONATOR
LIGHT SOLVENT
12
13
WILD NAPHTHA
11
SOUR WATER
14
COMBINED PRODUCT

9 - Scrubber Water - Water Scrubber Unit
10 - Rich DEA - DEA Scrubber
11 - Condensed Water from P-302 and P-304
12 - Light Solvent Fuel Oil
13 - Naphtha
14 - Combined Product from E-306

Figure 4. Solvent Hydrogenation Section

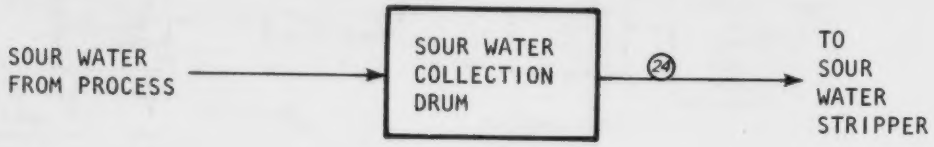
The rich DEA from the DEA scrubbers is pumped to the fuel gas treating and DEA regeneration section (Figure 5). The DEA is fed to the DEA regenerator, where it is stripped of H_2S and SO_2 and then returned to the process. The stripped acid gas is water scrubbed and sent to the refinery for sulfur recovery. The raw fuel gas is water scrubbed and then DEA scrubbed before being used as fuel gas for the process.


RICH DEA
15
RECYCLE GAS
WASH WATER
16
FUEL GAS TREATING AND DEA REGENERATION AREA
17
18
FUEL GAS TO PROCESS
19
LEAN DEA TO PROCESS
20
21
SOUR WATER
22
23
ACID GAS TO REFINERY

15 - Rich DEA - Hydrocarbon Skimming Drum
16 - Wash Water Input
17 - Offgas - Fuel Gas Condensate Separator Drum
18 - Offgas - Fuel Gas DEA Scrubber
19 - Lean DEA - DEA Regenerator
20 - Sour Water - Fuel Gas DEA Scrubber Sour Water Pump
21 - Scrubber Water - Acid Gas Water Scrubber
22 - Offgas - DEA Regenerator
23 - Acid Gas to Refinery

Figure 5. Fuel Gas Treating and DEA Regeneration Section

All of the sour water and scrubber water generated by the process is pumped to the sour water collection section (Figure 6). The sour water is then pumped to the refinery's sour water stripper.



24 - Sour Water - Sour Water Disposal Pump

Figure 6. Sour Water Collection Section

SAMPLING PROGRAM

PRE-SAMPLING ACTIVITIES

To accommodate a sampling effort of this size and scope, a field laboratory had to be established. The chosen facility was an empty, 2,500 sq.ft. warehouse located 1/2 mile from the pilot plant. This building was the central point for all sample splitting, preservation, packaging, shipping, and on-site analysis.

To reduce the work load for the field team, as much preparatory work as possible was done at the home office. A field manual was compiled which provided exact instructions on the handling, preservation, and shipment of each sample. Each sampling team member was assigned a specific task during the sampling effort. All sample bottles, 2,200 in all, were pre-cleaned and labeled before shipment to the field laboratory.

The on-site analysis called for the use of a gas chromatograph to analyze gaseous grab samples. These samples had to be analyzed within one hour after sampling in order to meet holding-time requirements. An experienced chemist with a GC background was assigned to these analyses.

All necessary equipment and chemicals were delivered to the field laboratory at least four days before sampling began. This provided time for the field team to check over the equipment and prepare any necessary reagents.

SAMPLING SCHEDULE

With the exception of the gaseous samples, samples were collected twice daily, at 8:00 a.m. and 8:00 p.m., on three consecutive days. Samples for the process variability program were collected during the appropriate sampling period along with the composite samples. The sampling schedule is detailed in Table 2.

TABLE 2. ECLP SAMPLING SCHEDULE

Day 1	Day 2	Day 3
A.M.	A.M.	A.M.
Composite Samples Process Variability Samples	Composite Samples Process Variability Samples	Composite Samples
P.M.	P.M.	P.M.
Composite Samples	Composite Samples	Composite Samples Process Variability Samples

Composite samples contained equal aliquots from all six sampling periods. The analytical result for each component from this composite is the average value of that component over the six sampling periods. Process variability samples are not composited but are distinct samples representing individual sampling periods. The analytical results from these samples track certain components to determine how the concentration varies with changing process conditions and other factors.

IN-PLANT AND FIELD LABORATORY ACTIVITIES

Liquid samples were collected in 5-gallon and 1-gallon bottles. The 5-gallon bottles were used to collect composite and process variability samples, while the 1-gallon bottles were used only for composite samples. Volatile Organic Analysis (VOA) samples were taken in 40 ml septum-top vials and sampled in duplicate. Feed coal and vacuum bottom samples were collected in 2-liter, brown-glass, wide-mouth bottles.

Once all the samples from a given sampling period were obtained, they were immediately returned to the field laboratory for processing. This phase included sample splitting and preservation. Samples from the 5- and 1-gallon bottles were split into smaller bottles for two reasons, first, to allow for required preservation steps, and second, to make sample handling easier for laboratory personnel. Thus, there was less chance for sample degradation and errors in handling and analysis. Each composite sample bottle and process variability sample bottle was pre-labeled. These labels contained the stream name, intended analysis, preservation method, and aliquot volume required. Having all the bottles labeled with the proper information enabled the field team to perform production-line sample splitting.

Preservation of the samples for shipment and subsequent analysis was very important. Every precaution was taken to properly preserve the samples and to reduce the degradation of the chemical species of interest.

Samples were preserved in accordance with the procedures defined in Manual of Methods: Preservation and Analysis of Coal Gasification Wastewaters, (Luthy, Richard G.). Each aliquot that was split into sample bottles had to be preserved, and most of the 2,200 samples required chemical preservation. These preservation procedures were repeated six times on approximately 1,500 bottles.

Packaging and shipment was the last procedure that the samples were subjected to at the field laboratory. Holding-time requirements dictated that the volatile organic analyses samples be delivered overnight to the analytical laboratory. The samples also had to be kept at 4°C during shipping to meet preservation requirements. The samples were packed in styrofoam shipping coolers with packing material and ice just prior to pickup by the shipper. To avoid the loss of a sample due to breakage in transit, all samples were prepared in duplicate and shipped so that duplicates were in separate coolers. Composite samples were stored in ice during the 3-day sampling period while compositing was being completed. With these packaging procedures, only four of the 2,200 bottles were lost or broken.

PROBLEM AREAS AND SOLUTIONS

There are many problems associated with a sampling effort of this size. The best way of avoiding difficulties is to identify potential problem areas and determine what precautions can be taken. Three areas which Hittman identified as potential problems were:

- Fumes and vapors from the acidification of sour water samples containing high levels of sulfur
- Keeping the samples at 4°C for an extended period of time
- Properly packaging and shipping the samples.

Since acidification with concentrated nitric or sulfuric acid is required for several species, any evolution of H_2S from the samples could present a health hazard. A glove box was converted into a sealed-hood system with vacuum pumps to draw the gas out of the box and through two scrubbing bottles containing 15 to 25% NaOH. The scrubbed gas was pumped to the outside of the field laboratory. Industrial fans were located so that H_2S fumes and other hazardous materials were prevented from accumulating in the field laboratory.

Samples were kept in a large walk-in dumpster converted into a cooler. Layers of 1-inch polystyrene were attached to the walls and floor and covered with thick plastic. A roof was installed and insulated with polystyrene and plastic. The dumpster was 24 feet long, 6 feet wide, and 4 feet high. It required between 800 and 1,000 pounds of block ice per day to keep the samples at 4°C. Refrigerated trucks were not suitable because of the danger of contamination in the event of a sample spill.

The packaging and shipment of such a large quantity of bottles is subject to both mishandling and breakage. This problem was addressed by having the samples duplicated, split, and shipped in different coolers. In this way, if a cooler was lost in shipment or damaged, sufficient sample would still be available in the other cooler. Two members of the sampling team were assigned full-time to packaging and coordinating sample shipments.

ANALYTICAL PROGRAM

The EDS analytical program consisted of two areas: composite sample analysis and variability sample analysis. The analyses of the composite samples included a wide range of chemical tests, while the variability analyses were limited to four tests. Results from the composite samples will provide an overall picture of the plants operation during the three days of sampling. Results from the process variability samples will provide information on the sensitivity of certain species to process variations.

The analyses performed on the composite samples are listed in Table 3.

TABLE 3. EDS COMPOSITE SAMPLE ANALYSES

Inorganics and Water Quality Parameters

CN^-	Cl^-	TSS	Phenolics	BOD
NH_3+	Fl^-	TDS	Oil & Grease	Trace Metals
$S^=$	Alkalinity	Total N	TOC	SCN^-
NO_2/NO_3	Acidity	Total S	COD	SO_4:

Organics		Bioassays	
VOA	GC/FID	Ames Test	RAM Test
GC/MS	HPLC	CHO Cytotoxicity	Fathead Minnow
			Daphnia

The variability analyses performed are listed in Table 4.

TABLE 4. EDS PROCESS VARIABILITY ANALYSES

Total sulfur
Total Nitrogen
Trace Metals
GC/FID
Organics
GC/MS

These analyses will aid in defining the cause of differences in test results due to process and sampling variability, analytical accuracy, and analytical reproducibility.

Process variability is the result of variations in process operating parameters during the sampling period. Variations are due to changes in coal feed rate, solvent recycle rate, temperature, pressure, and other operational parameters. If the plant has not reached process equilibrium before sampling is initiated, sample variability will result from non-steady state conditions.

Sampling variability results from non-reproducibile samping technique (e.g., non-isokinetic sampling or sampling of non-homogeneous streams).

Analytical variability in precision results from non-homogeneity of sample, minor variations in technique, etc., while variability in accuracy is normally the result of poor recoverability during extractions.

The determination of the variability due to these four factors is illustrated in the branch diagram in Figure 7.

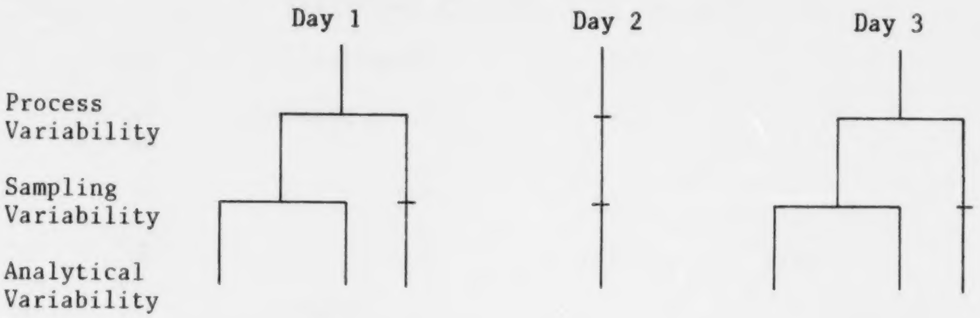


Figure 7. Process Variability Branch Diagram

The application of this diagram can be more clearly seen when analytical results are presented with it (Figure 8).

PRELIMINARY RESULTS

Preliminary results for the sample sour water - atmospheric fractionator are presented in Table 5. This stream is the condensed water from the reflux drum of the atmospheric fractionator. A process block diagram of this sample is provided in Figure 2, Product Distillation Area. The results are from the six-period composite sample.

In the Source Test Evaluation Report on the EDS pilot plant, all results will be presented as a range. This range will be determined on the basis of the analytical error derived from the variability analyses.

		DAY 1 AM			DAY 2 AM	DAY 3 PM			
		(a)	(b)	(c)		(a)	(b)	(c)	detection limit
Aluminum	Al	0.22	0.25	L	0.23	0.28	0.24	0.25	0.15
Antimony	Sb	L	L	L	L	L	L	L	0.15
Arsenic	As	0.004	0.003	0.004	0.003	0.003	0.003	0.003	0.002
Barium	Ba	0.023	0.020	0.024	0.020	0.025	0.025	0.027	0.001
Beryllium	Be	L	L	L	L	L	L	L	0.003
Bismuth	Bi	L	L	L	L	L	L	L	0.50
Boron	B	474.	480.	486.	454.	448.	452.	468.	0.01
Cadmium	Cd	L	L	L	L	L	L	L	0.025
Calcium	Ca	0.92	0.89	0.91	0.95	0.89	0.86	0.96	0.01
Chromium	Cr	L	0.082	L	0.14	L	0.040	L	0.03
Cobalt	Co	L	L	L	L	L	L	L	0.02
Copper	Cu	L	L	L	0.038	L	L	L	0.015
Iron	Fe	1.42	0.35	0.32	0.22	0.20	0.20	0.25	0.03
Lead	Pb	L	L	L	0.10	L	L	L	0.08
Magnesium	Mg	0.089	0.091	0.078	0.110	0.095	0.098	0.110	0.001
Manganese	Ma	0.060	0.026	0.021	0.019	0.019	0.014	0.015	0.003
Mercury	Hg	0.112	0.097	0.087	0.086	0.098	0.088	0.088	0.002
Molybdenum	Mo	L	L	L	L	L	L	L	0.04
Nickel	Ni	0.058	0.031	L	0.043	0.027	L	L	0.025
Phosphorus	PO_4	L	L	L	L	L	L	L	0.40
Potassium	K	0.38	2.92	0.37	0.45	0.38	0.49	0.56	0.01
Selenium	Se	-	-	-	-	-	-	-	
Silicon	SiO_2	4.64	3.82	2.76	4.45	4.52	3.30	5.21	0.08
Silver	Ag	L	L	L	L	L	L	L	0.03
Sodium	Na	1.60	1.72	1.90	2.32	1.66	1.74	2.11	0.10
Strontium	Sr	L	0.004	0.003	0.004	L	L	0.003	0.001
Tin	Sn	L	L	L	L	L	L	L	0.03
Titanium	Ti	L	L	L	L	0.010	0.029	0.010	0.006
Tungsten	W	-	-	-	-	-	-	-	
Uranium	U	-	-	-	-	-	-	-	
Vanadium	V	L	L	L	L	L	L	L	0.01
Zinc	Zn	0.068	0.088	0.066	0.240	0.110	0.150	0.072	0.015

(- = cannot be analyzed by ICAP)
(L = less than detection limit)
(All units are mg/l)

Figure 8. ICAP Analysis of Sour Water From Recycle Gas Cold Separator Drum, Process Variability EDS Samples

TABLE 5. PRELIMINARY ANALYTICAL RESULTS, SOUR WATER - ATMOSPHERIC FRACTIONATOR

Water Quality Parameters	Concentration (mg/l)
COD	93,700
TOC	27,000
TDS	678
TSS	31
Alkalinity (as $CaCO_3$)	5,020
Cl^-	122
Fl^-	8
NH_3	1,730
$S^=$	188
Oil and Grease	<20
NO_3	0.15
$SO_4^=$	63
SCN^-	240
Phenolics	18,000
Aluminum	0.024
Boron	0.054
Calcium	2.61
Iron	1.90
Magnesium	0.085
Potassium	0.16
Sodium	2.16
Zinc	0.091
Total S	1,640
Total N	1,990

Organic Analysis - Major Components

GC/MS - Acid and Base/Neutral Extracts Analysis

Phenol

C_1 Phenol

C_2 Phenol

Aniline/Methyl Pyridine

Benzofuran

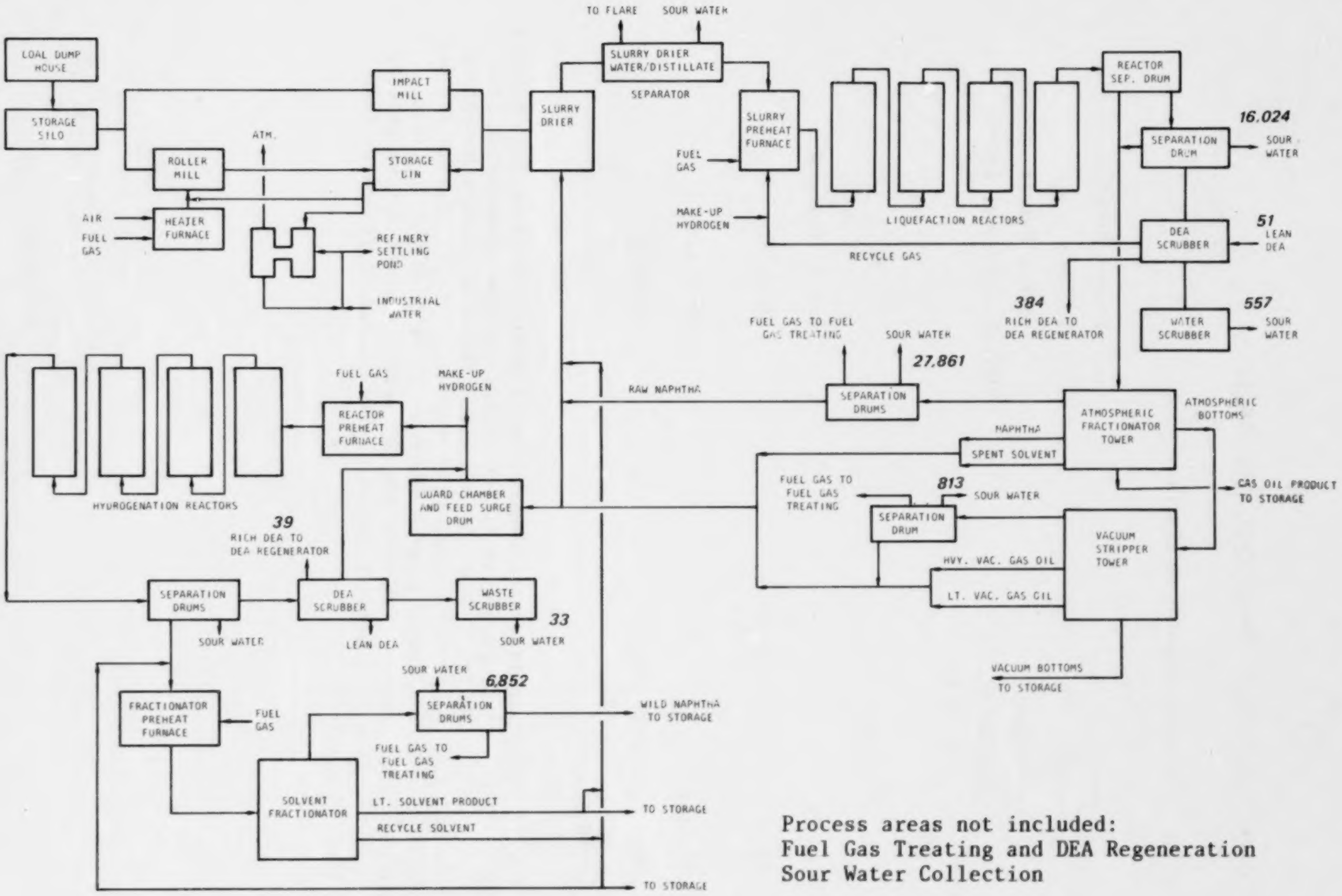
Organic Analysis - Major Components (Continued)

GC/MS - Volatile Organic Analysis

Butane
Pentane
C-6 Alkanes
C-7 Alkanes
Ethyl Nitrile
Propyl Nitrile
Toluene
Methyl Pyrole
Methyl iso-butyl ketone

Bioassays	EC_{50}
Ames Test	Not determined
CHO Clonal Cytotoxicity Assay	<6 ul/ml
RAM Assay	<6 ul/ml
Fathead Minnow (LC_{50})	0.047%
Daphnia	0.158%

Figure 9 represents the concentration of phenolics in several process streams. The level of phenolics is the highest in the condensates from the separation drums throughout the process. The sour water-atmospheric fractionator has the highest level of phenolics. Several streams are not represented in this process diagram, such as those from the fuel gas treating and DEA regeneration area and the sour water collection section. These omitted streams generally contain lower levels of phenolics than indicated in Figure 9.


COAL DUMP HOUSE
STORAGE SILO
IMPACT MILL
ROLLER MILL
STORAGE BIN
ATM.
AIR
FUEL GAS
HEATER FURNACE
REFINERY SETTLING POND
INDUSTRIAL WATER
SLURRY DRIER
TO FLARE
SOUR WATER
SLURRY DRIER WATER/DISTILLATE
SEPARATOR
SLURRY PREHEAT FURNACE
FUEL GAS
MAKE-UP HYDROGEN
LIQUEFACTION REACTORS
RECYCLE GAS
REACTOR SEP. DRUM
16.024
SEPARATION DRUM
SOUR WATER
51
DEA SCRUBBER
LEAN DEA
384
RICH DEA TO DEA REGENERATOR
557
WATER SCRUBBER
SOUR WATER
FUEL GAS TO FUEL GAS TREATING
SOUR WATER
27,861
SEPARATION DRUMS
RAW NAPHTHA
ATMOSPHERIC FRACTIONATOR TOWER
ATMOSPHERIC BOTTOMS
NAPHTHA
SPENT SOLVENT
GAS OIL PRODUCT TO STORAGE
FUEL GAS TO FUEL GAS TREATING
813
SOUR WATER
SEPARATION DRUM
VACUUM STRIPPER TOWER
HVY. VAC. GAS OIL
LT. VAC. GAS OIL
VACUUM BOTTOMS TO STORAGE
HYDROGENATION REACTORS
FUEL GAS
REACTOR PREHEAT FURNACE
MAKE-UP HYDROGEN
GUARD CHAMBER AND FEED SURGE DRUM
39
RICH DEA TO DEA REGENERATOR
SEPARATION DRUMS
SOUR WATER
DEA SCRUBBER
LEAN DEA
WASTE SCRUBBER
33
SOUR WATER
FRACTIONATOR PREHEAT FURNACE
FUEL GAS
SOUR WATER
6,852
SEPARATION DRUMS
WILD NAPHTHA TO STORAGE
FUEL GAS TO FUEL GAS TREATING
SOLVENT FRACTIONATOR
LT. SOLVENT PRODUCT
RECYCLE SOLVENT
TO STORAGE
TO STORAGE

Process areas not included:
Fuel Gas Treating and DEA Regeneration
Sour Water Collection

Figure 9. Phenolics in EDS Pilot Plant Process (mg/l)

SUMMARY

A pilot plant is not fully representative of a commercial facility. To obtain the most representative data possible, we sampled only those streams which we know will be present in a commercial facility. Streams that are unique to the pilot plant were not sampled. The results obtained from the analyses of these samples can be scaled up based on the expected operational conditions of a commercial-scale facility.

The process variability analyses performed as part of this program were mainly a quality control/quality assurance measure. The data obtained from the process variability analyses will be evaluated to determine the accuracy and precision of the analytical results. By identifying the source of variations in the data, it is possible to reduce errors in future sampling and analytical programs.

ACKNOWLEDGEMENTS

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PB83-128264

HEALTH AND ENVIRONMENTAL STUDIES OF H-COAL PROCESS*

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ABSTRACT

With the implementation of the Energy Security Act of 1980, coal and oil shale are expected to be principal sources for petroleum and natural gas substitutes. H-Coal is one of several processes under intensive study for the direct conversion of coal to the desired synthetic fuels.

In this paper we describe the health and environmental study program of H-Coal, sponsored by the Department of Energy. Presented are the results of the chemical, biological, and ecological characterization of products and by products derived from the operation of a process development unit. These initial results provide an informed basis for subsequent monitoring and testing activities of the nominal 200- to 600-ton/d pilot plant at Catlettsburg, Kentucky.

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HEALTH AND ENVIRONMENTAL STUDIES OF H-COAL PROCESS

INTRODUCTION

In the next two decades the major production and use of products derived from coal and oil shale is expected. The primary incentive for such development is the imbalance between the domestic supply and demand for oil and gas and the consequent dependence on oil imports.[1] Clearly a synthetic fuels (synfuels) industry will increase flexibility in dealing with any future disruptions in the world oil market.

Over 70 coal liquefaction processes have been proposed.[2] These can be classified as indirect liquefaction, direct liquefaction, and pyrolysis. The Department of Energy (DOE) is devoting considerable attention to direct liquefaction because of its potential for lower cost. H-Coal is one of the attractive methods of reacting coal with hydrogen in the direct production of liquid products such as naphtha and fuel oils.

Accompanying the development of energy-producing technologies is the consideration of potential health and environmental impacts. Recognizing this need, DOE asked Oak Ridge National Laboratory (ORNL) to develop comprehensive environmental and health plans to study the H-Coal process and in particular the pilot plant at Catlettsburg, Kentucky. Components of the pilot plant operation applicable to commercial size facilities are to be emphasized. Similar studies of the solvent refined coal (SRC) process are in progress elsewhere, complementing the H-Coal activity. Together they will provide a basis for technology assessments.[3]

Our study of the H-Coal process is being carried out in two phases. Phase I involves characterizing and testing materials produced by a process development unit (PDU); Phase II is a study of the pilot plant. In this paper we report the results of our Phase I activities and describe the Phase II program, which has just begun.

PROCESS DESCRIPTION

H-Coal is a process for the catalytic hydrogenation of coal under high pressure and temperature to produce liquid hydrocarbon products and fuel gas. The process was developed initially by Hydrocarbon Research, Inc., with the use of bench-scale units and a 3-ton/d PDU located in Trenton, New Jersey. A pilot plant was subsequently constructed at Catlettsburg, Kentucky, with a nominal capacity of 200- to 600-ton/d, depending upon the operating mode. Operation of the plant began in 1980 to demonstrate the commercial viability of the process and develop data for the design of commercial units.

In the H-Coal process (Figure 1), coal is slurried with a process-derived oil, pumped to reactor pressure, mixed with recycle and makeup hydrogen, and fed through a preheater to the catalytic (Co/Mo) ebullated-bed reactor. Typical operating conditions are 2500-3000 psi and 850°F. Catalyst activity is maintained by the periodic addition of fresh catalyst and the withdrawal of spent catalyst, and ebullition is provided by an external pump that recycles the coal-solvent slurry.

The reactor products leave the reactor and are separated for subsequent processing. The vapor from the reactor is cooled and scrubbed to produce a H_2-rich recycle gas and a light hydrocarbon stream fed to the distillation unit. The liquid-solid product from the reactor, containing unconverted coal, ash, and oil, is fed to a liquid flash separator. The flashed-off material is passed to the distillation unit to produce a variety of fuel gases and light and heavy distillate products. The bottoms products from the flash separator are further separated in a hydroclone and then in a vacuum distillation unit. A portion of the heavy distillate is recycled to the reactor, with the heavy bottoms stream from the vacuum distillation unit being utilized for hydrogen production.

By varying the residence time in the reactor, the process can be designed to operate in the synthetic crude (syncrude) or the fuel oil mode. To produce syncrude, more hydrogen is required and there is a lower yield of residual fuel oil. To produce a low-sulfur residual fuel oil as a major product, the temperature and pressure in the reactor are lower and less hydrogen is required. However, a special liquid-solid separation unit, not shown in Figure 1, will be required.

PROCESS DEVELOPMENT UNIT STUDIES

Elements of our synfuels research program concern the chemical, physical, and biological properties of hazardous or toxic materials; the environmental transport and systems to control the release of or to minimize the exposure to such materials; and the assessment of the consequences of exposure. Numerous comparative studies of coal-derived liquids and other related materials such as shale oils, petroleum crude oils, petroleum products, and various polynuclear aromatic compounds have been completed and reported, including research with materials from the H-Coal PDU.[4]

The following discussion is limited to the results of several of the more recent characterization and testing studies of samples from the PDU. These samples are not necessarily representative of coal liquids that will eventually be produced in a commercial facility; consequently they are not adequate for definitive process-specific comparisons. The results are valuable, however, as indicators of potential problem areas. As such, they provide a basis for selecting samples and defining studies to be performed with pilot plant materials.

Characterization and Cellular Bioassays

An important focal point of our research has been the identification of

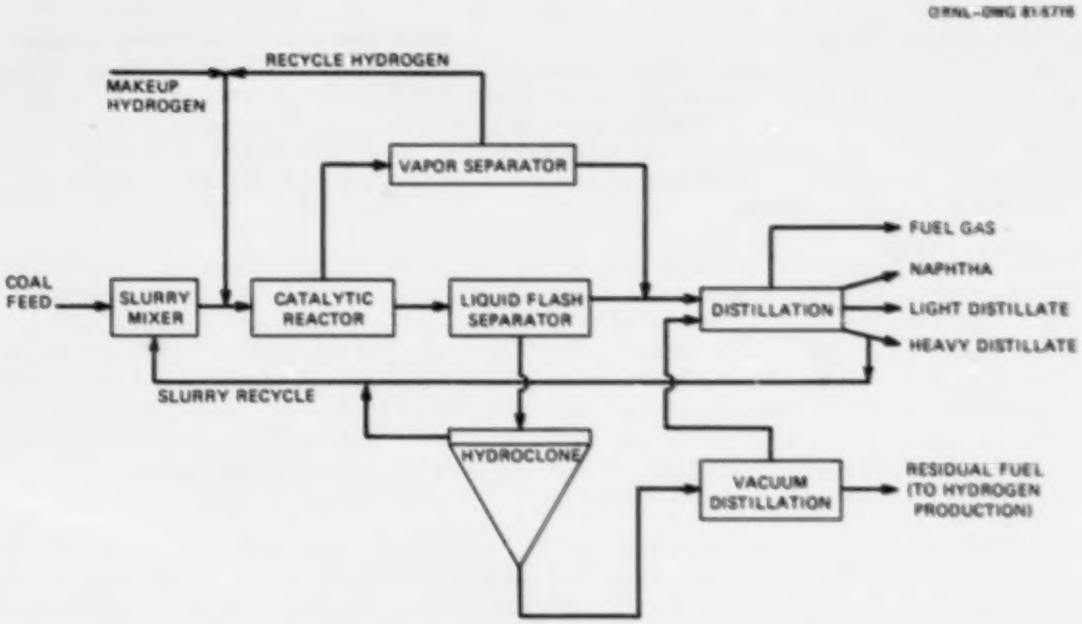

ORNL-DWG 81-6716
RECYCLE HYDROGEN
MAKEUP HYDROGEN
VAPOR SEPARATOR
FUEL GAS
NAPHTHA
COAL FEED
SLURRY MIXER
CATALYTIC REACTOR
LIQUID FLASH SEPARATOR
DISTILLATION
LIGHT DISTILLATE
HEAVY DISTILLATE
SLURRY RECYCLE
HYDROCLONE
VACUUM DISTILLATION
RESIDUAL FUEL (TO HYDROGEN PRODUCTION)

Figure 1. H-Coal Process Schematic.

the chemical constituents responsible for the potential biological effects of synfuel products and processing effluents. An effective approach is to integrate biological testing with a chemical manipulation of the test material. Thus, in our comparative mutagenesis program we have emphasized the combining of chemical class fractionation with biotesting.

Samples examined in this study were provided by Mobil Research and Development Corporation and Hydrocarbon Research, Inc., and incorporated into the Synfuels Research Materials Facility.[5] Both raw distillates and products upgraded by hydrotreatment (HDT) were included. The samples are identified in Table 1, with information given on their boiling point ranges and ultimate analyses. Because these samples were not necessarily representative of the coal liquids that will eventually be produced in a commercial facility, they were used for generic research into the chemical and biological properties of petroleum substitutes.

All samples were treated according to the procedure shown in Figure 2. After removal of the highly volatile matter, the residue was fractionated into chemical classes with a diethyl ether-aqueous acid partitioning and a subsequent Sephadex LH-20 separation of the neutral fraction.[6,7] The resulting volatiles, insoluble matter, and acidic, basic, and neutral subfractions were weighed and subjected to bacterial mutagenic testing. Although biological screening studies with H-Coal materials have included tests in a bacterial system (Salmonella typhimurium) and a protozoan system (Tetrahymena pyriformis),[8] only the former tests are discussed in this paper.

The results of characterization and mutagenic testing are summarized in Table 2 by general chemical class and approximate weight and by mutagenic contribution. These results, useful in identifying general trends as opposed to absolute hazards posed by the test materials, have been discussed extensively in other publications.[9,10] For example, the total mutagenicities (the sum of chemical fractions) of coal-liquid samples that are more volatile (sample No. 1312) or that have been hydrotreated (sample Nos. 1603 and 1604) tend to be lower, and mutagenicity tends to increase with increasing vapor pressure (e.g., sample Nos. 1313-1315). These samples exhibit greater mutagenicity than petroleum crude oils. In addition to the neutral subfractions, the alkaline components can contribute significantly to the mutagenicity of coal liquids. Recent evidence indicates that polycyclic aromatic amines and azaarenes are unusually bioactive alkaline constituents whereas polar-substituted neutral polycyclic aromatics are occasionally responsible for high mutagenicities.

In-Vivo Mammalian Tests

Whole-animal studies have included the preliminary investigation of both the acute and chronic toxic effects of coal-derived liquid materials. A total of five acute toxicity tests was used: determination of the acute toxicity following oral and interperitoneal administration of the test materials to mice, acute dermal toxicity in rats, primary skin irritation and eye irritation in rabbits, and delayed-contact sensitivity in guinea pigs. Skin carcinogenesis tests involved the repeated application of the test material to the shaved skin of mice. Test and data analyses procedures have been described elsewhere.[11,12]

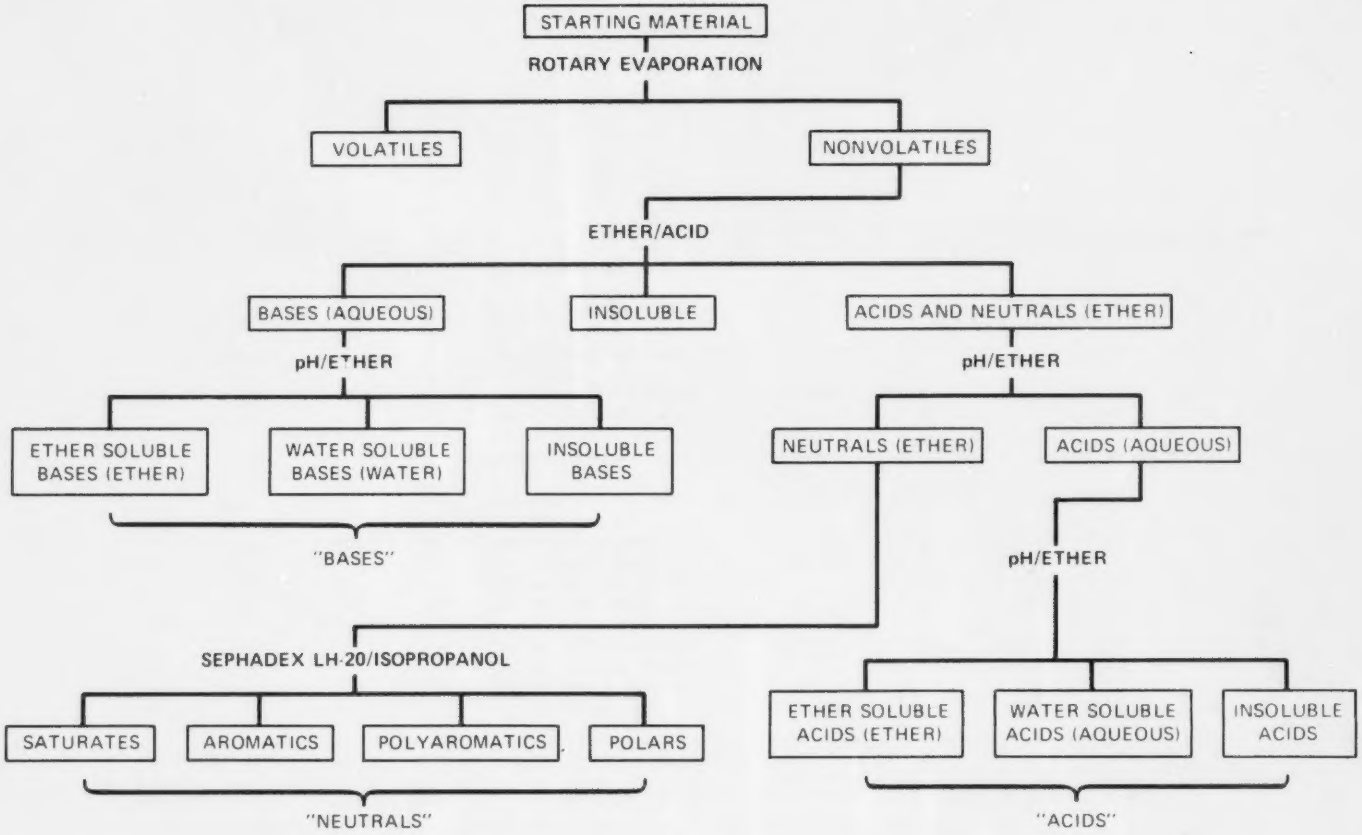
TABLE 1. PROPERTIES OF COAL LIQUID SAMPLES FROM PROCESS DEVELOPMENT UNIT

Identification		Operational		Description	Characteristics					
					Boiling*	Wt. %				(%)**
PDU Run	ORNL Repository	Mode	Coal	Sample Point Location	Range(°F)	Hydrogen	Oxygen	Nitrogen	Sulfur	C_A
1	1601	Fuel oil	Ill. No. 6	H-Coal distillate (raw)	300-700	9.65	1.62	0.39	0.107	57
	1602			HDT at low severity		9.87	0.95	0.20	0.002	52
	1603			HDT at medium severity		10.5***	0.39	0.13	<0.002	45
	1604			HDT at high severity	200-650	10.9***	0.21	0.09	<0.002	39
1		Fuel oil	Ill. No. 6	H-Coal fuel oil	375-1000					58
	1617			HDT at low severity		9.17	0.94	0.58	0.059	52
	1618			HDT at medium severity		9.22	0.74	0.55	0.039	51
	1619			HDT at high severity	375-1000	9.67	0.44	0.30	0.011	44
5	1308	Syncrude	Ill. No. 6	Atmospheric overhead (ASOH)	146-590	11.8		0.17	0.07	
	1309			Atmospheric bottoms (ASB)	458-650 (66%)	9.4		0.37	<0.03	
	1310			Vacuum overhead (VSOH)	492-650 (34%)	8.7		0.42	<0.03	
	1311			Vacuum bottoms (VSB)		4.3		0.90	3.0	
7	1312	Fuel oil	Ill. No. 6	Atmospheric overhead (ASOH)	172-565	11.4		0.30	0.2	
	1313			Atmospheric bottoms (ASB)	410-650 (81%)	9.5		0.40	0.5	
	1314			Vacuum overhead (VSOH)	462-633 (46%)	8.7		0.50	0.1	
	1315			Vacuum bottoms (VSB)		4.7		1.5	2.2	

*Parenthetical values are percent of volume distillated at highest indicated temperature.

**Aromatic carbon as percent of total carbon.

***Estimated.


STARTING MATERIAL
ROTARY EVAPORATION
VOLATILES
NONVOLATILES
ETHER/ACID
BASES (AQUEOUS)
INSOLUBLE
ACIDS AND NEUTRALS (ETHER)
pH/ETHER
pH/ETHER
ETHER SOLUBLE BASES (ETHER)
WATER SOLUBLE BASES (WATER)
INSOLUBLE BASES
NEUTRALS (ETHER)
ACIDS (AQUEOUS)
"BASES"
pH/ETHER
SEPHADEX LH-20/ISOPROPANOL
SATURATES
AROMATICS
POLYAROMATICS
POLARS
ETHER SOLUBLE ACIDS (ETHER)
WATER SOLUBLE ACIDS (AQUEOUS)
INSOLUBLE ACIDS
"NEUTRALS"
"ACIDS"

CHEMICAL CLASS FRACTIONATION FOR BIOTESTING

MATERIAL, **STEP**, (PHASE)

Figure 2. Swain-Stedman Acid-Base Fraction Coupled with LH-20 Separation of Neutral Fraction

TABLE 2. APPROXIMATE MUTAGENICITY AND WEIGHT DISTRIBUTIONS BY CHEMICAL CLASS

	Mutagenic Activity*					Weight Distribution				
		Percentage Contribution				Percent of Total				
Sample	Total (revert mg-1)	Acids	Bases	Neutrals	Other**	Acids	Bases	Neutrals	Other**	Total Recovered
H-Coal ASB (Syn) No. 1309***	970	1	46	53	0	<1	3	95	<1	99
H-Coal VSOH (Syn) No. 1310	2400	0	42	58		1	3	95	1	100
H-Coal VSB (Syn) No. 1311	2000	0	66	17	16	2	5	30	65	102
H-Coal ASOH (FO) No. 1312	0	0	0	0		1	2	55	35	93
H-Coal ASB (FO) No. 1313	140	0	100	0		1	2	95	1	99
H-Coal VSOH (FO) No. 1314	4200	0	25	75		1	2	95	1	99
H-Coal VSB (FO) No. 1315	6300	0	89	9	2	1	10	30	60	101
H-Coal 'Dist' No. 1601	350	0	37	63	0	1	1	85	4	91
H-Coal 'Dist' HDT-L No. 1602	540	0	0	100	0	1	2	85	10	98
H-Coal 'Dist' HDT-M No. 1603	210	0	0	100	0	1	2	80	10	93
H-Coal 'Dist' HDT-H No. 1604	0	0	0	0	0	1	1	80	15	97
Wilmington Crude No. 5301	5	0	0	100	0	2	1	90	7	99

*Determined using *S. typhimurium* strain TA98 and Arochlor-1254-induced rat liver microsome preparation.

**Volatiles and precipitates other than acidic and basic precipitates.

***Numbers following sample names are designations of the ORNL repository. Abbreviations are identified in Table 1.

Consult Ref. 10 for test results with other coal-derived, shale-derived, and petroleum crude oils.

The results of the acute oral toxicity tests are listed in Table 3.[13] The LD_{50}s of the PDU materials were greater than those of the petroleum crude oil, but only of moderate toxicity. The trend suggests that oral toxicity tends to be lower for the more volatile and HDT coal liquids. No coal liquid tested exhibited acute lethality in rats when applied to the skin at a dose of 2 g/kg or produced skin sensitization when applied intradermally. Eye irritation was noted with some materials, although it was a reversible effect.[14]

Chronic dermal exposure studies revealed that coal liquids from the PDU were carcinogenic to mouse skin.[15] The most carcinogenic materials were those of higher boiling range, but a substantial reduction of skin carcinogenic potential occurred even at the lowest severity of hydrotreatment involved. Neurotoxic and systemic toxic effects are now being studied.

Ecological Tests

Parallel studies of the acute and chronic effects of PDU materials on aquatic and terrestrial organisms of different ecological organizational levels have also been completed.[16,17] This discussion will be limited to the test results of liquid products in bioassays with freshwater algae (*Selenastrum capricornutum* and *Microcystis aeruginosa*) and freshwater crustacean (*Daphnia magna*), the basic screening tools for preliminary comparative studies.

Spills of liquid products derived from coal, oil shale, and natural petroleum are a potential source of environmental impact. Comparative information on transport, dissolution and effects is necessary to define the potential impacts and the requirements for cleanup. Of considerable interest is the primary toxic materials which dissolve rapidly into water in the event of an aquatic spill. Thus, one element of research has focused on water-soluble fractions (WSFs) of these materials; the results of testing several PDU materials are listed in Table 4.

The WSFs permit testing of the toxic components of oils, which were prepared by gently stirring the mixture of oil floating on distilled water. Their effect on photosynthesis by freshwater algae was measured as a concentration causing 20% inhibition (EC_{20}) of organic carbon uptake in 4-h exposures.[18] Values for the coal-liquid WSFs were below those for petroleum WSFs or of greater potential acute toxicity. Water soluble fractions were also tested for acute toxicity to *Daphnia* in standard 48-h bioassays (LC_{50}) and for chronic effects in examinations of the lowest concentrations at which significant change to reproduction was observed in 28-d exposures (LOEC).[19,20] The acute effects for the WSFs of coal liquefaction products were larger (LC_{50}s ranging from 0.2 to 4.6%) than those for the petroleum products; similarly, reproduction effects were also larger.

Generally the toxicity of chemical class fractions from coal-liquid WSFs was found to increase as ether-soluble bases > ether-soluble acids > neutral subfractions. Phenolic compounds and anilines were determined to be the most important water soluble components of the coal liquids in terms toxic effects.

TABLE 3. ACUTE TOXICITY IN MAMMALIAN SYSTEM

Sample	Oral LD_{50}* (g/kg)	95% Confidence Limits
H-Coal ASB (Syn) No. 1309**	3.6	2.4-5.2
H-Coal VSOH (Syn) No. 1310	2.5	1.7-3.1
H-Coal ASOH (FO) No. 1312	5.8	4.7-7.2
H-Coal ASB (FO) No. 1313	2.3	1.9-2.6
H-Coal ASOH (FO) No. 1314	2.6	2.2-3.2
H-Coal 'Dist' No. 1601	3.6	2.8-4.5
H-Coal 'Dist' HDT-L No. 1602	4.0	3.4-4.7
H-Coal 'Dist' HDT-H No. 1604	5.5	2.8-7.2
Wilmington Crude No. 5301	>16	

*Dose in grams of material per kilogram of body weight that kills 50% of animals.

**Numbers following sample names are designations of the ORNL repository. Abbreviations are identified in Table 1.

TABLE 4. TOXICITY IN ECOLOGICAL TEST SYSTEMS

Sample	Algae Acute Toxicity		Crustacea Toxicity	
	(EC_{20})*		Acute (LC_{50})**	Chronic (LOEC)***
	Selenastrum capricornutum	Microcystis aeruginosa	Daphnia magna	Daphnia magna
H-Coal ASOH (Syn) No. 1308****	0.25	0.46		
H-Coal ASB (Syn) No. 1309	0.30	0.26	4.6	0.58
H-Coal VSOH (Syn) No. 1310	0.063	0.13	2.5	0.92
H-Coal ASOH (FO) No. 1312	0.019	1.4	0.24	0.016
H-Coal ASB (FO) No. 1313	0.16	0.15	1.0	0.25
H-Coal ASOH (FO) No. 1314	0.019	0.13	2.5	
H-Coal 'dist' No. 1601	0.42	0.91	0.4	
H-Coal 'dist' HDT-L No. 1602	0.57	0.75	0.5	
H-Coal 'dist' HDT-M No. 1603	0.68	1.4	1.5	
H-Coal 'dist' HDT-H No. 1604	0.60	1.6	1.7	
Petroleum No. 2 diesel fuel	15.	25.	30.	20.

*WSF concentration (percent dilution) causing 20% inhibition of photosynthesis.

**WSF concentration (percent dilution) that killed 50% of the organisms in 48-h.

***Lowest WSF concentration (percent dilution) at which significant effects on reproduction were observed in 28-d.

****Numbers following sample names are designations of the ORNL repository. Abbreviations are identified in Table 1.

PLANNED STUDIES OF PILOT PLANT

Major areas of health and environmental concern for synfuel development have been described in detail.[21-24] These include consideration of facility siting, potential degradation of air and water quality, solid waste management, worker health and safety, and potential public health risks. Extensive federal legislation exists to cope with these concerns, with the new legislation having increased almost exponentially in number since the passage of the National Environmental Policy Act of 1969.[25] However, additional information in these areas is needed; thus, research programs relate to the perceived issues involving both regulated activities and yet-to-be-defined regulations.

The objective of the H-Coal Environmental and Health Program is to provide data and information to support analyses and assessments of coal liquefaction technology. It is not intended as an environmental compliance activity, because the protection of the worker and environment at the pilot plant is the responsibility of Ashland Synthetic Fuels, Inc. (ASFI).

Program emphasis is on those aspects of the H-Coal process and those units that can conceivably be scaled to commercial-size facilities. Process sampling is thus keyed to the examination of products, effluents, possible occupational exposures, and the information necessary for control technology evaluation. Biological screening activities focus on samples representing material of the greatest potential for human exposure or health effects, tempered with the results of tests on samples from the H-Coal PDU. Environmental studies complement the process and in-plant studies, with the thrust on testing product oils and plant effluents, including solid wastes.

PROCESS MEASUREMENTS AND CONTROLS

Sufficient samples and analyses are provided to characterize a few points in the process streams and nearly all the points of plant effluents and to assess the efficiency of environmental control devices. The details of process sampling and analyses are described in the H-Coal program plan.[26] In general, process sampling strategy provides for the characterization of materials introduced into the process; minimal sampling of intermediate-process streams based on considerations of mass flow, scale-up problems, and the potential for occupational exposure; and final product and waste streams.

Fifty-three sampling points are located to meet our sampling criteria; twenty-four are built into the plant (e.g., hydroclone overhead), and the others can be obtained at several preselected points (e.g., coal pile runoff). Sample collection is targeted to steady-state operation, and because steady-state operation cannot be determined a priori, several sample suites will be collected during each coal run. After operational conditions are evaluated, materials for testing are selected from samples that have been stored under controlled conditions. The frequency and intensity of sampling and monitoring are subject to modification as experience dictates.

The analytical procedures and the constitutents or parameters to be measured were chosen to allow early measurement of traditionally monitored or suspected materials and to maximize the likelihood of detecting unexpected and hazardous constituents. Results must be adequate to document process conditions, to evaluate the efficiency of environmental control technology, to identify limitations in sample size or analytical methodologies, to identify possible biological hazards in potential fugitive emissions, and to assign priorities to materials for subsequent bioassay.

Each sample can be identified as a process sample, a product (or final effluent), a fugitive emission, or a solid waste. As shown in Table 5, each sample is designated a process (I), product (II), fugitive emission (III), or solid-waste (IV) sample. Subsets of each category--gases, tars, solids, etc.-- can then be listed with the chemical and physical characterizations to be performed. Thirty-two classes of analyses are specified, but not for all samples. For example, the study of oils and tars comprises (1) elemental analysis; (2) analyses of Environmental Protection Agency (EPA) priority pollutant trace elements; (3) determination of filterable solids, moisture, volatile organic compounds, volatile organosulfur compounds, benzo(a)pyrene, polycyclic aromatic hydrocarbons, and organonitrogen compounds; (4) organic class analyses; and (5) a bioassay preparation. As with sampling, we view the analyses strategy as flexible because actual measurements may suggest curtailing some studies or expanding others.

Environmental Control Technology--

A complete evaluation of two environmental control methods that are scalable to larger systems will be attempted. One is the diethanolamine absorption towers for CO_2 and H_2S removal from the sour fuel gas and vent gas streams, the other is the sour water strippers for H_2S and NH_3 removal from the wastewater stream. Companion studies will also be made of the remaining wastewater system with the operating contractor. A special study of the treatability of coal liquefaction wastewaters (described below) will also be undertaken.

Sample Collection Status--

Present plans are to operate the pilot plant in the syncrude operational mode with at least three different coals. During a 45-d run initiated on February 17, 1981, using Illinois No. 6 coal, two sets of samples were collected and placed in storage. Early in May the plant was brought on stream with a Kentucky No. 9 coal, and an extensive sample set was taken for the environmental program. Limited characterization and testing of these latter samples began in late August. During September continuous plant operation with Illinois No. 6 coal was achieved, and two additional sample sets were collected. As this run continues, additional samples will be collected. Selection between these sets for subsequent study will be made shortly on the basis of process conditions.

OCCUPATIONAL EXPOSURE AND EFFECTS

The potential exposure of man in the working environment includes consideration of plant area controls and the effects on man if exposures occur. Monitoring and testing activities thus involve the requirements of worker protec-

TABLE 5. DETERMINATIONS CONSTITUTING THE STUDIES

Study	Ultimate analysis[a]	EPA priority elements[b]	EPA drinking water elements[c]	Anionic analysis	Leachable elements	Filterable solids	Total suspended solids	pH	Total organic carbon	Moisture	Extractable organics[d]	XAD-2 extractables - GC/MS analysis	Volatile organic compounds	Volatile organo-sulfur cmpds.	H_2S	SO_2	Stable gases	BaP	Total particulate loading	Leachable organics	Sulfur: organic, pyritic, sulfate	PAHs	Organonitrogen compounds	Organohalogen compounds	Size fractionation	Standard drinking water tests	Organic class analysis	Texax adsorbables[f]	Bioassay preparation	Direct GC/MS analysis	Area samplers[g]	EP[h] extract preparation
Process (I)																																
Solids (IA)	X	X																			X											
Oils and tars (IB)	X	X				X				X			X	X				X				X	X				X		X			
Process waters (IC)			X	X			X	X	X			X[d]																	X			
Oily waters (ID)			X	X			X	X	X		X	X[d]															X		X			
Gases (IE)												X	X	X	X	X	X											X				
Product (II)																																
Solids (IIA)	X	X			X						X							X		X									X			
Naphtha and light oils (IIB)	X	X											X	X															X	X		
Fuel oils (IIC)	X	X											X	X	X	X	X	X				X	X				X		X			
Gases (IID)		X[e]									X[e]	X	X	X					X			X[e]	X[e]					X	X[e]			
Processed water (IIE)												X														X						
Fugitive emissions (III)																																
Solids (IIIA)		X									X								X						X				X			
Liquids (IIIB)	X	X				X				X			X	X				X				X	X				X		X			
Gases (IIIC)																															X	
Solid wastes (IV)	X	X								X	X		X									X		X			X		X			X

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[a] C, H, N, S, O.

[b] Ag, As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, Tl, and Zn; also includes Co and Mo plus any other elements which are easily determined by the techniques used.

[c] As, Ba, Cd, Cr, Pb, Hg, Se, Ag.

[d] Includes extractables from suspended solids.

[e] Pertains to the particulate content.

[f] Analysis for chemical smog precursors (e.g., acetaldehyde).

[g] Standard components determined in industrial hygiene surveillance.

[h] EP: RCRA protocol extraction procedure (EPA).

tion and the potential effects of exposure to primary effluents and fugitive emissions.

Plant Area Sampling and Characterization

The primary objective of an industrial hygiene program is to recognize, evaluate, and control exposures that may have the capability of producing untoward health effects. ASFI has prime responsibility for protecting the health of its employees, and we have participated by complementing ASFI's requirements and providing information for occupational health control assessments.

Two types of monitoring of potential exposures are provided. Area monitoring for particulates, fugitive emissions, and various physical and chemical stresses indicates possible exposures whereas personnel monitoring defines the actual exposures. New capabilities in monitoring pollutants associated with tars and oils have been demonstrated and will be used in program implementation.[27] These include portable instruments with the real-time measurement capabilities listed in Table 6 to assist in the selection of sample sites and in the determination of residual worker contamination. A variety of standard industrial hygiene techniques employing filter cassettes and gas badges will also be used to define the time-weighted exposures to organic vapors and particulate contamination.

Occupational Toxicology

The principal focus of our occupational toxicology studies is on the testing of products, primary effluents, and potential fugitive emissions to estimate the effects on man. Questions to be answered concern:

- the relative toxicity of products, by-products, and effluent;
- toxicity variation with process conditions; and
- the potential for work-place toxicity.

A tiered or multilevel approach will be used in the investigation of these questions of toxicity, which will be guided by the results with PDU materials. Level one tests, or cellular mutagenic bioassays, are the initial screens to ascertain the relative toxicity of materials of interest and the need for further testing and to correlate with whole-animal somatic effects. Level two tests, or mammalian somatic toxicity tests, complement the mutagenic and cytotoxic testing and provide validating or confirmatory information on biological potency.

In Table 7 we list the bioassays to be employed, although not all tests will be run on all samples collected at a given point. Cellular bioassays make use of a variety of biological systems including bacteria, yeast, and mammalian cells to investigate mutagenic effects. These shorter-term tests will provide guidance in subsequent testing and be complemented by longer-term validating assays using Drosophila, cultured mammalian cells, and whole-animal (mouse) systems. Toxicity tests involve the use of whole animals to characterize the acute, subacute, and chronic toxicity of products and effuents. They are used in the study of materials of likely high toxicity

TABLE 6. PORTABLE MONITORING INSTRUMENTS

Control Pollutant	
NH_3, NO_x, SO_2, C_6H_6, C_6H_5OH, naphthalene its derivatives	Second-derivative ultraviolet absorption spectrometer with multipass gas cell for real-time monitoring of selected effluents
Tar and oil on contaminated surfaces	Fluorescence spill spotter for general surface contamination including BaP
Tar and oil on contaminated skin	Lightpipe luminoscope for residual skin contamination using very low intensities of UV light
PNA vapors	Passive meter for area or personnel monitoring of selected PNA compounds using room-temperature phosphorescence detection techniques

TABLE 7. BIOASSAY TESTS FOR HEALTH EFFECTS ASSESSMENT

Purpose	Test
Screening	1. Bacteria-- *Salmonella typhimurium* strains
	2. Yeast-- *Saccharomyces cerevisiae*
	3. DNA repair-- *Bacillus subtilis*
	4. Mammalian cell (CHO) cytotoxicity
	5. Invertebrate cytotoxicity-- *Tetrahymena pyriformis*
	6. Embryo toxicity-- *Xenopus laevis*
	7. Mammalian teratogenesis-- mouse
Screening and validation	1. Fruit fly-- *Drosophila melanogaster*
	2. Mammalian cell (CHO) gene mutation
	3. Mammalian cell (CHO) cytogenetic damage
	4. Mammalian cell (leukocyte) chromosomal change
	5. In-vitro cell transformation
Mammalian mutagenesis	1. Mouse-- dominant lethals
	2. Mouse-- heritable translocations
	3. Mouse-- specific locus
	4. Mouse-- spot test, somatic mutation
	5. Mouse-- reproductive capacity
Mammalian toxicity	1. Mouse-- acute oral LD_{50}
	2. Mouse-- intraperitoneal injection LD_{50}
	3. Rat-- acute dermal toxicity
	4. Rabbit-- eye and skin irritation
	5. Guinea pigs - dermal sensitization
	6. Mouse-- maximum tolerated dose
Mammalian carcinogenesis	1. Mouse-- lung tumors
	2. Mouse-- skin tumors

about which little information is available but which have potential for human exposure. A brief description of each bioassay is provided in the H-Coal program plan.

ENVIRONMENTAL FATE AND EFFECTS

Environmental studies emphasize the data base requirements to assess the H-Coal technology rather than the pilot plant. Consequently, the thrust of the program is on characterizing and testing process and plant effluents, solid wastes, and liquid products. The latter studies are concerned with the effects of possible oil spills on terrestrial and aquatic systems.

Ecological tests to be performed on the various materials are identified in Table 8. Toxicity screening tests provide an initial indication of potential ecological effects and include algal photosynthetic inhibition (4-h exposure) and acute toxicity response (48-h LC_{50}), the latter using three different aquatic test organisms. Materials showing high toxicity and high potential for environmental exposure will be tested further. These activities include tests of the reproduction effects on crustacea and insects and of acute toxicity and abnormalities on fish embryo-larval life stages. Chemical and physical characterization (Table 1) is a part of the testing protocol.

The transport and fate of products that may be spilled in aquatic environments will be studied in small field ponds. Aqueous extracts of vacuum bottoms flaked product and filter cake consisting of solids from the wastewater treatment system will be prepared to simulate on-site storage and landfill disposal, respectively, and will be subjected to selected tests. Studies of aqueous wastes will be limited to effluents from the wastewater treatment plant and to the combined discharge (process water, sanitary effluents, and sursurface runoff from the plant site) to the Big Sandy River. All tests will be replicated with equivalent petroleum crude and oil for comparison purposes.

SPECIAL STUDIES

Several special studies will be carried out to examine issues of particular importance in direct coal liquefaction, which involves the H-Coal process. They are summarized as follows.

Advanced Wastewater Control Technology

A 1-gpm wastewater treatment PDU will be designed and constructed for initial use at the H-Coal pilot plant.[28] The treatment unit provides the means to evaluate the efficiency and cost of advanced treatment techniques to achieve zero stream discharge or meet future discharge regulations, to investigate the operational problems of existing systems, and to provide scale-up data for larger facilities. Unit processes in the treatment train will be constructed in transportable, self-contained modules that can be interchanged or bypassed to achieve maximum flexibility. As shown in Figure 3, unit processes will provide for pretreatment and conditioning by distillation stripping of NH_3 and H_2S, setting and flotation for solids and oil removal, and solvent extraction for phenol removal; biological oxidation; and polishing operations

TABLE 8. ECOLOGICAL TESTS OF H-COAL MATERIALS

Sample Description	Photosynthesis, algal-- Selenastrum capricornutum and Microcystis aeruginosa	Acute toxicity, crustacea -- Daphnia magna	Acute toxicity, midge larva— Chironomus tentans	Acute toxicity, fathead minnow-- Pimephales promelas	Reproduction, crustacea-- Daphnia magna	Reproduction, cricket-- Acheta domesticus	Embryo-larval toxicity, fathead minnow— Pimephales promelas	Transport studies
Light fuel oil*	X	X	X	X	X	X***	X	X***
Heavy fuel oil*	X	X	X	X**	X**		X**	X***
Vacuum bottoms, flaked product*	X	X			X**			
Treated process wastewater	X	X	X	X	X		X**	
Filter cake*	X	X	X	X	X**		X**	X***
Combined aqueous discharge	X	X						
Petroleum crude* ****	X	X	X	X	X	X***	X	X***

*Aqueous extract unless otherwise indicated.

**Tests to be performed if chemical characterization or Daphnia acute toxicity indicates potential hazard.

***Whole oil tested rather than aqueous extract.

****For comparison with H-Coal liquid products.

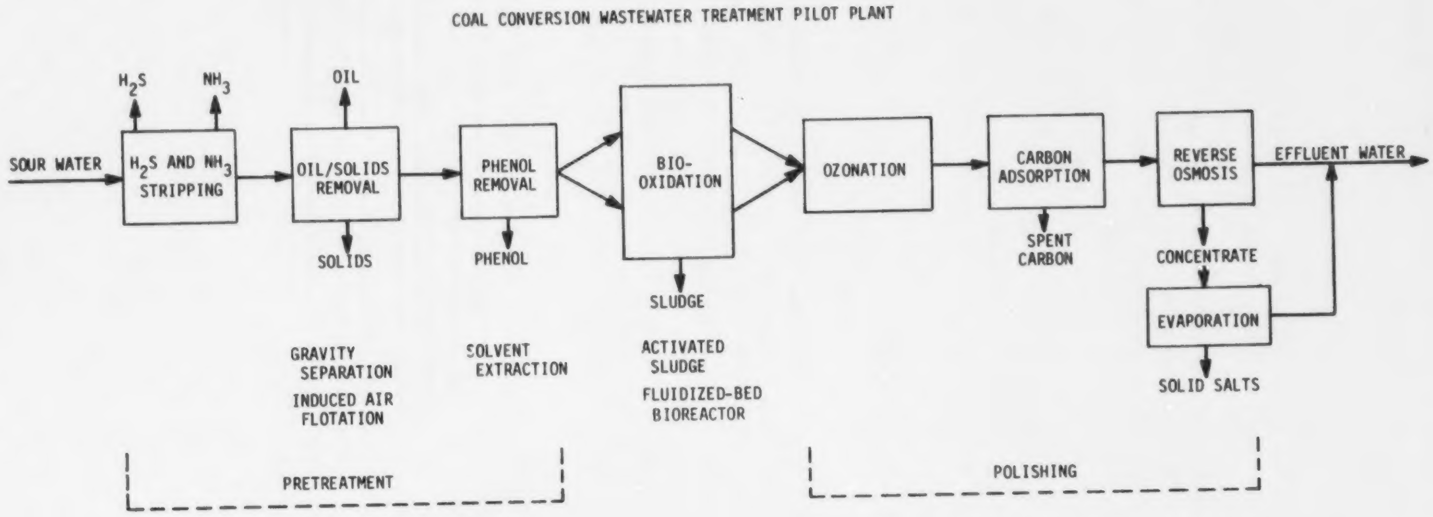
COAL CONVERSION WASTEWATER TREATMENT PILOT PLANT
SOUR WATER
H_2S
NH_3
H_2S AND NH_3 STRIPPING
OIL
OIL/SOLIDS REMOVAL
SOLIDS
PHENOL REMOVAL
PHENOL
BIO-OXIDATION
SLUDGE
OZONATION
CARBON ADSORPTION
SPENT CARBON
REVERSE OSMOSIS
EFFLUENT WATER
CONCENTRATE
EVAPORATION
SOLID SALTS
GRAVITY SEPARATION
INDUCED AIR FLOTATION
SOLVENT EXTRACTION
ACTIVATED SLUDGE
FLUIDIZED-BED BIOREACTOR
PRETREATMENT
POLISHING

Figure 3. Coal Conversion Wastewater Treatment Process Development Unit

with ozonation and carbon adsorption for refractory and residual organic removal and reverse osmosis for dissolved salt removal.

Product Upgrading

Exploratory research indicates that hydrotreatment and selective distillation of H-Coal PDU liquid products may reduce significantly microbial genotoxicity and mammalian toxicity. Similar findings are reported for SRC-II liquids.[29] Consequently, a systematic study has begun of the effects of hydrotreatment and process conditions on the chemical, physical, and biological properties of liquid products derived from pilot plant operations of H-Coal, SRC-II, and Exxon Donor Solvent (EDS) processes. Blends of distillates will be hydrotreated to three levels of severity and characterized and tested for toxicological response. In a companion effort the status and preliminary cost estimates of process technology for hydrotreatment, boiling-cut fractionation, and other methods of product upgrading (e.g., nitrosation, acid-base extraction, organic solvent extraction, and chromatographic separation) will be investigated.[30]

CONCLUDING REMARKS

Samples of coal-liquid products from the H-Coal PDU have provided initial information on important areas of continuing research. Comparative studies show that crude petroleum substitutes, including the H-Coal materials, generally exhibit greater activity in biological and ecological test systems than petroleum crudes, but this activity is reduced in samples that have been hydrotreated and in low-boiling distillates. Constituents of the alkaline and neutral fractions of coal liquids are responsible for mutagenicity whereas phenolic compounds and anilines cause the greatest toxicity in freshwater algae and zooplankton.

Based upon the initial results of studies with PDU materials and in consideration of the scale-up requirements for a commercial-size facility, the implementation of an extensive health and environmental study of the H-Coal pilot plant has begun. Plans include the characterization and testing of products, by-products, and effluents; collaborative studies with the operating contractor involving plant area monitoring and worker protection; and investigations of environmental controls for plant effluents. Systematic studies have also begun of hydrotreatment and other methods of upgrading liquid products to alleviate biological activity.

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CHEMICAL CHARACTERIZATION AND BIOASSAY OF SRC PROCESS MATERIALS

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ABSTRACT

Bioassay techniques have shown that certain coal liquefaction process streams and products are both mutagenic (Ames assay) and carcinogenic. These materials have been chemically fractionated using a number of techniques (solvent extraction, alumina column separation, HPLC, Sephadex LH-20) in an attempt to identify the constituents responsible for the biological activity. These studies have shown that primary aromatic amines (PAA's) account for more than 90% of the mutagenic response in the Ames test. Long-term skin painting and initiation-promotion assays indicate that the PAA's may also play a role in the carcinogenicity of the coal-derived materials. However, while the PAA's can be designated as the determinant mutagens in coal liquids, they cannot be assigned a determinant role in skin carcinogenesis. Thus far, carcinogenicity appears to better correlate with increasing molecular weight and boiling point. Our results also suggest that benzo(a)pyrene is not a reliable marker compound for carcinogenic activity.

(Only the abstract is published herein.)

Session II: WATER-RELATED ENVIRONMENTAL CONSIDERATIONS

Chairman: N. Dean Smith
U.S. Environmental Protection Agency
Research Triangle Park, NC

Cochairman: William E. Corbett
Radian Corporation
Austin, TX

COAL CONVERSION WASTEWATER TREATMENT/REUSE - AN OVERVIEW

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ABSTRACT

Environmentally, the production of synfuels from coal can be classified into two categories: (1) low temperature processes, and (2) high temperature processes. Low temperature processes are characterized by the production of high boiling liquids and tars which tend to retain the multiple-ring structure of the original coal "molecule," while high temperature processes typically produce synthesis gas, methane and/or light liquids. Dry-ash moving-bed gasification and direct 1-quefaction processes are representative of low temperature conversion processes. Entrained gasification is an example of high temperature processes. Fluid bed gasification processes that operate at temperatures just below the ash slagging point may produce limited heavy liquids and fall intermediate within the classification regime.

Depending on the process, process steam which is subsequently condensed and/or gas clean-up quench waters come into direct contact with the raw gaseous product stream. As a consequence, the resultant wastewater associated with the low temperature processes is highly contaminated with organics. The production of ammonia in the high temperature processes is generally suppressed and reduced due to "cracking." Condensate waters from high temperature processes usually contain little or neglible NH_3, while the condensate waters from low temperature processes contain high levels of NH_3. The condensate waters from both low and high temperature processes generally contain volatized and entrained mineral matter, trace elements and salts as well as adsorbed H_2S, CO_2, and cyanates.

The treatment of the condensate waters from the low temperature processes poses a special challenge due to the high and variable level and toxic nature of the gross organics. A portion of the total organic carbon is biorefractory and this also causes concern. Laboratory treatability tests have demonstrated that with appropriate dilution and/or pretreatment (e.g., gas stripping, organic extraction, and/or the addition of powdered activated carbon) activated sludge treatment processes do a reasonable job of reducing biological oxygen demands (BOD) and total organic carbon levels (TOC), and coupled with activated carbon treatment, relatively high quality effluent can be produced. In a "zero discharge" mode, subsequent concentration and reuse of the effluent must be effected to ultimately produce a concentrated brine or dry salt.

The questions that remain center on the capability of this rather elaborate treatment train to accommodate variabilities in the raw feed and on the reliability and costs of such a system, i.e., do viable alternatives exist? Options will be outlined with special emphasis on: (1) improvements to biological treatment, and (2) purely physical/chemical systems. The effect of more stringent standards with respect to, say, the control of biorefractory ring-structure compounds, trace elements, ammonia, etc., will be discussed relative

to the state-of-the-art biotreatment and these environmental control options. Areas of uncertainty and future research will be delineated based on a recent synfuel wastewater workship, conducted in June 1981.

INTRODUCTION

The capability to adequately treat and discharge wastewaters associated with coal conversion causes some apprehension primarily because of the lack of treatability data from actual operating facilities, at scale and under stringent discharge standards. A number of concerns exist for the tentative wastewater control systems:

- the possible requirement to meet tighter future effluent discharge standards for ring-structured biorefractory organics, trace elements, ammonia, etc.;
- the high level of contamination, variability of composition, and large and variable volumeric flowrate (variability being a special concern with pioneer type plants);
- the vulnerability of biological treatment systems to toxic effects (either due to high loadings in the feed and/or build-up of toxic agents from recycle); and
- the desirability that the wastewater treatment/reuse system be highly reliable to preclude shutdown or curtailment of production.

If one considers "chemical" pollutants of universal concern, adverse environmental effects include (1) changes in pH by strong acid and bases, (2) increase in water corrosivity and reduced suitability for irrigation due to soluble salts, (3) toxicity caused by heavy metals, phenols and cyanides, (4) depletion of dissolved oxygen by oxygen consuming organics, (5) surface films from trace oils, (6) taste and odor problems associated with phenols and chlorinated derivatives and (7) release of biorefractory materials which can be fatal to fish and aquatic life (note--the effect on man, especially any long term cumulative effects, has not been established).

Representative compositions of condensate waters resulting from low temperature coal conversion processes contain each of these "chemical pollutants" (Figure 1). It is apparent that intensive and specialized treatments are required for such waters.

In the design of wastewater treatment facilities, a variety of sources are encountered, although condensate waters typically account for over half the wastewater produced (Figure 2). General design practice is to segregate streams and use different methods of pretreatment tailored to the composition of the individual streams. The current pollution control design data base is such that the practice is to encourage the incorporation of of enhanced design flexibility within the total system. In this context, "flexibility" refers to parallel units and/or spares, conservative design specifications, bypass lines and space to accommodate additional equipment, if necessary. If one examines the preliminary designs of a number of wastewater treatment trains, one finds a high degree of variation between individual process designs with provisions for "flexibility" reflecting a common design philosophy (Figures 3, 4, 5).

	GASIFICATION	DIRECT LIQUEFACTION		
	LURGI	SRC I	H-COAL	EDS
pH	9.0-9.5	8.4	9.5-10.8	–
BOD	4,000-15,000	17,000	–	–
TOC	4,000-20,000	11,000	–	–
COD	15,000-30,000	80,000	28,000	–
PHENOLS	2,000-6,000	1,900	70,000	6,000
SULFIDE, S	100-600	16,000	30,000	12,000
AMMONIA, N	2,000-10,000	18,000	15,000	9,500
THIOCYANATE, SCN^-	20-200	–	–	10
CYANIDE, CN^-	0.1-10.0	–	4.0	4.0
TDS	1,000-5,000	15,000	–	–

FIGURE 1. COMPOSITION OF REPRESENTATIVE RAW CONDENSATE WATERS FOR "LOW TEMPERATURE" CONVERSION PROCESSES, PPM

WASTEWATER STREAM	SOURCE	QUANTITY Mgpd	MAJOR CONCERN
PROCESS CONDENSATE			
HIGHLY CONTAMINATED (LOW TEMPERATURE PROCESSES)	MOVING BED GASIFIERS DIRECT LIQUEFACTION	1.5-7.0 .05-1.0	ORGANICS
MODERATELY CONTAMINATED (HIGH TEMPERATURE PROCESSES)	ENTRAINED GASIFIERS	2.5-4.0	–
	FISCHER TROPSCH,* MOBIL-M*	1.0-3.0	ORGANICS
CLEAN	METHANATION STEP	0.2-1.0	–
BLOWDOWNS			
COOLING TOWER	COOLING TOWER SYSTEM	0.5	TDS
BOILER	ION EXCHANGE REGENERATION AND REVERSE OSMOSIS CONCENTRATE	0.1-1.0	
RAIN RUNOFF	RAIN FALL FROM IMPOUNDMENT	VARIABLE	MIXED
SANITARY WASTES	POTABLE WATER SYSTEM	75% POTABLE RATE	

*EXCLUSIVE OF GASIFICATION STEP

FIGURE 2. SUMMARY OF COAL CONVERSION PLANT WASTEWATER STREAMS (3×10^{11} Btu/d REF PLANT)

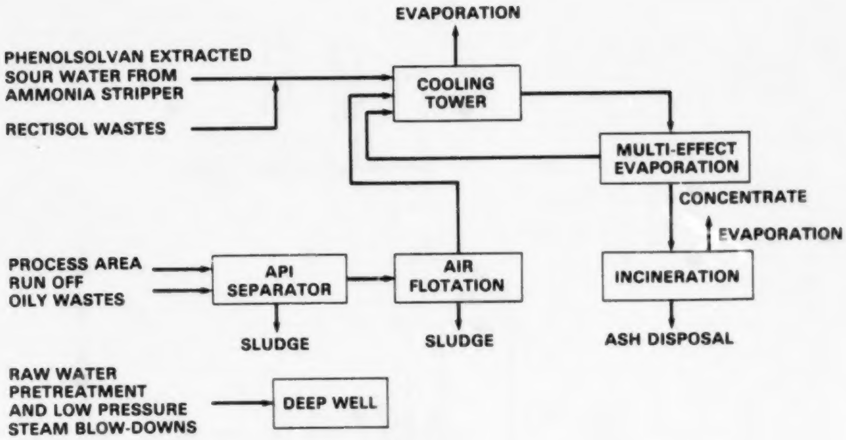
EVAPORATION
PHENOLSOLVAN EXTRACTED SOUR WATER FROM AMMONIA STRIPPER
RECTISOL WASTES
COOLING TOWER
MULTI-EFFECT EVAPORATION
CONCENTRATE
EVAPORATION
PROCESS AREA RUN OFF
OILY WASTES
API SEPARATOR
AIR FLOTATION
INCINERATION
SLUDGE
SLUDGE
ASH DISPOSAL
RAW WATER PRETREATMENT AND LOW PRESSURE STEAM BLOW-DOWNS
DEEP WELL

FIGURE 3. WASTEWATER TREATMENT SYSTEM ANG COAL GASIFICATION PLANT

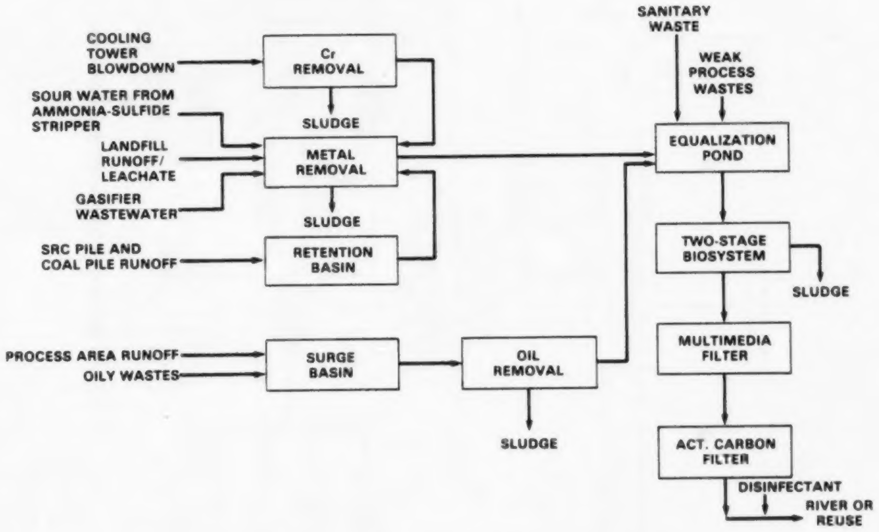
COOLING TOWER BLOWDOWN
Cr REMOVAL
SLUDGE
SOUR WATER FROM AMMONIA-SULFIDE STRIPPER
LANDFILL RUNOFF/ LEACHATE
METAL REMOVAL
GASIFIER WASTEWATER
SLUDGE
SRC PILE AND COAL PILE RUNOFF
RETENTION BASIN
SANITARY WASTE
WEAK PROCESS WASTES
EQUALIZATION POND
TWO-STAGE BIOSYSTEM
SLUDGE
MULTIMEDIA FILTER
PROCESS AREA RUNOFF
OILY WASTES
SURGE BASIN
OIL REMOVAL
SLUDGE
ACT. CARBON FILTER
DISINFECTANT
RIVER OR REUSE

FIGURE 4. TENTATIVE WASTEWATER TREATMENT SYSTEM—
SRC-I DEMONSTRATION PLANT

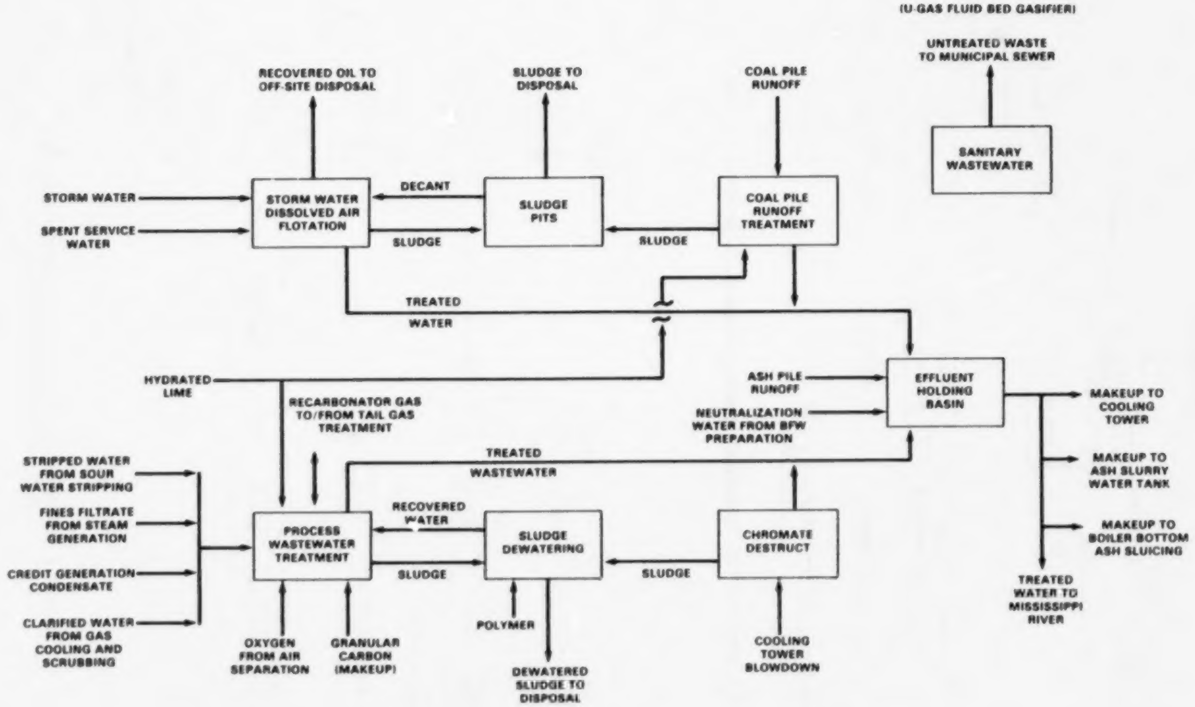
(U-GAS FLUID BED GASIFIER)
RECOVERED OIL TO OFF-SITE DISPOSAL
SLUDGE TO DISPOSAL
COAL PILE RUNOFF
UNTREATED WASTE TO MUNICIPAL SEWER
SANITARY WASTEWATER
STORM WATER
SPENT SERVICE WATER
STORM WATER DISSOLVED AIR FLOTATION
DECANT
SLUDGE
SLUDGE PITS
SLUDGE
COAL PILE RUNOFF TREATMENT
TREATED WATER
HYDRATED LIME
RECARBONATOR GAS TO/FROM TAIL GAS TREATMENT
ASH PILE RUNOFF
NEUTRALIZATION WATER FROM BFW PREPARATION
EFFLUENT HOLDING BASIN
MAKEUP TO COOLING TOWER
MAKEUP TO ASH SLURRY WATER TANK
MAKEUP TO BOILER BOTTOM ASH SLUICING
TREATED WATER TO MISSISSIPPI RIVER
TREATED WASTEWATER
STRIPPED WATER FROM SOUR WATER STRIPPING
FINES FILTRATE FROM STEAM GENERATION
CREDIT GENERATION CONDENSATE
CLARIFIED WATER FROM GAS COOLING AND SCRUBBING
RECOVERED WATER
PROCESS WASTEWATER TREATMENT
SLUDGE
SLUDGE DEWATERING
SLUDGE
CHROMATE DESTRUCT
OXYGEN FROM AIR SEPARATION
GRANULAR CARBON (MAKEUP)
POLYMER
DEWATERED SLUDGE TO DISPOSAL
COOLING TOWER BLOWDOWN

FIGURE 5. WASTEWATER TREATMENT SYSTEM — MEMPHIS INDUSTRIAL FUEL GAS PLANT

DESIGN BASIS FOR WASTEWATER TREATMENT TRAIN

While there are many options for the wastewater treatment/reuse systems, several criteria are overriding in determining the characteristics of the raw influent and the ultimate basis of design:

- geographical location of the plant (i.e., availability of water supply and nature of effluent acceptor);
- characteristics of conversion process; and
- environmental setting and/or controlling permits/standards.

These criteria are obviously interdependent. The geographical location also determines the coal type and influences the product/by-product mix as called for by the market place; this in turn dictates the configuration of the plant. The site specific environmental constraints also influence the process design--the type and nature of wastewater treatment system; the propensity for wastewater reuse and disposal options for wastewater sludges (both organic and inorganic).

GEOGRAPHIC SITING

Geographical water availability/discharge constraints strongly influence the design philosophy for water use integral to the plant. In the arid West, dry cooling and staged quenching may be considered to conserve water, while "zero discharge," coupled with evaporation ponding, is likely to be encouraged to preserve salt-taxed river basins. In the East a different situation prevails; while the use of effluent discharge is considered to provide an acceptable means of salt dispersion, the release of residual trace biorefactory material and trace elements into potential drinking water supplies even though highly diluted, causes anxiety. This is especially true for biological-activated-sludge treatment systems which may experience upsets and require extended periods (several weeks) to recover. During the recovery period, adequate contingency must be available (holding ponds, plant derating, activated carbon units, etc.) to allow the plant to continue to operate.

The large coal requirements and concomitant ash disposal needs for commercial synfuel facilities dictates that the plant be located at or near the mine. There are significant chemical and processing differences between the western and eastern coals. While it is recognized that there are large and overlapping variations in the composition and chemistry of different coal types and that pretreatments can modify the coal structure, decrease ash and reduce sulfur and nitrogen levels, some generalizations relative to plant siting and feed stock requirements for the process can be made:

> Western (lignite and sub-bituminous type coals) are geologically younger than the eastern bituminous coals. The lignites, in particular, contain high levels of moisture and inherently produce net water during conversion. In the East, the ready availability of water supplies and discharge acceptors makes once-through water use preferred, although ideally the conversion processes can be

designed to be a net water consumer. The bituminous coals have agglommerating properties that generally preclude their use in moving bed gasifiers without intensive pretreatment. As a consequence, the large scale gasification of eastern bituminous coal will likely rely on entrained and/or fluid-bed gasifiers with a concomitant improvement in the quality of process condensate waters. Condensate waters associated with direct liquefaction processes will contain gross organic contamination for all coal types.

The composition of the runoff from coal storage piles is likely to vary as function of coal pyrite content. The pyrite abets acid generation which enhances the mobility of metals and total dissolved solids (TDS). The higher pyritic coals are in the East, thus potentially aggrevating a concern in a region where "zero discharge" is not contemplated. Ferric iron tends to predominate the metal release (Figure 6). Conventional treatment practice is neutralization followed by settling.

PROCESS CHARACTERISTICS

The reaction conditions and coal type in the conversion process strongly affect the composition of the condensate water. The most important variable is the temperature-residence time regime to which the coal/reaction products are exposed. This is markedly illustrated by comparing condensate water qualities for an entrained gasifier (bench scale) and a slagging moving bed gasifier (pilot-scale) (Figure 7). While the residence time in entrained gasifiers is very short (on the order of 20 millisec in the Eyring unit), the very high temperatures obtained appear capable of precluding the formation of ring-structured compounds and ammonia during a rapid devolatization/pyrolysis step. At the onset, the extremely rapid exothermic carbon-oxygen reaction predominates the slower endothermic steam-carbon and carbon dioxide-carbon reactions (Figure 8, regions I and II, respectively). The residual char has been demonstrated to effectively scavenger for trace ring-structured compounds that may be formed--the condensate water has been found to be nearly devoid of organics. This is in marked contrast to the condensate waters associated with lower temperature processes such as direct liquefaction with residence times up to several hours, which can contain practically all the organic compounds found in the coal. Thus, from the standpoint of raw condensate water quality and subsequent amenability to treatment, the temperature of coal conversion processes represents a major variable and the condensate waters may be classified under low or high temperature regimes.

A major variable effecting the low-temperature processes is coal rank--the more easily pyrolyzed, more reactive lignite and sub-bituminous western coals generally produce more phenols, given similar process conditions (Figure 9).

Process configurations, quantity and recycle of product gas quench waters and/or staging also determines the quantity and quality of the condensate waste stream. General gross differences between gasification and liquefaction condensate waters are reflected in the sulfide and ammonia concentrations (Figure 1). With respect to organics, laboratory treatability testing of steam stripped waters indicates that biological substrate utilization rates for liquefaction condensates may be significantly (an order of magnitude or more) less than gasification. The incentive for staged quenching and concomitantly reducing water requirements have been found to reside mainly in the use of less expensive materials of construction (carbon steel instead of stainless) downstream of the initial quench which removes the strong acids. Coals with a halide content of 0.15% Cl or greater, generally eastern coals, are expected to benefit from such a configuration.

PARAMETER	MEAN, PPM	RANGE, PPM
pH	2.7	2.1-3.0
IRON	20,000	0.2-90,000
SULFATE	9,000	500-22,000
ZINC	3.6	1.6-23
COPPER	2.1	1.6-3.4
CHROMIUM	3.3	0-16
TDS	16,000	720-44,000

FIGURE 6. REPRESENTATIVE COMPOSITION COAL PILE RAIN RUNOFF, EASTERN COAL
(ANDERSON AND YOUNGSTROM, CORNELL UNIVERSITY)

	HIGH TEMPERATURE	LOW TEMPERATURE
PROCESS	ENTRAINED	SLAGGING-MOVING BED
COAL TYPE	BITUMINOUS	LIGNITE
ORGANIZATION	EYRING RESEARCH (MOUNTAIN FUEL)	GFETC
pH	–	8.6
BOD	NIL	26,000
TOC	NIL	11,000
COD	–	32,000
PHENOLS	NON-DETECTED (<5)	5,500
SULFIDE, S	1.5	100
AMMONIA, N	35 (FIXED)	6,000
THIOCYANATE	–	120
CYANIDE	.02 MAX	2
TDS	330	2400

*NOTE–ABSOLUTE CONCENTRATIONS ARE DEPENDENT ON QUENCH WATER CONTACT/RECYCLE ETC. WHICH DIFFER. RELATIVE PREDOMINANCE OF SPECIES IMPORTANT.

FIGURE 7. COMPARISON OF CONDENSATE WATER FROM "HIGH TEMPERATURE" AND "LOW TEMPERATURE" GASIFICATION PROCESSES, PPM*

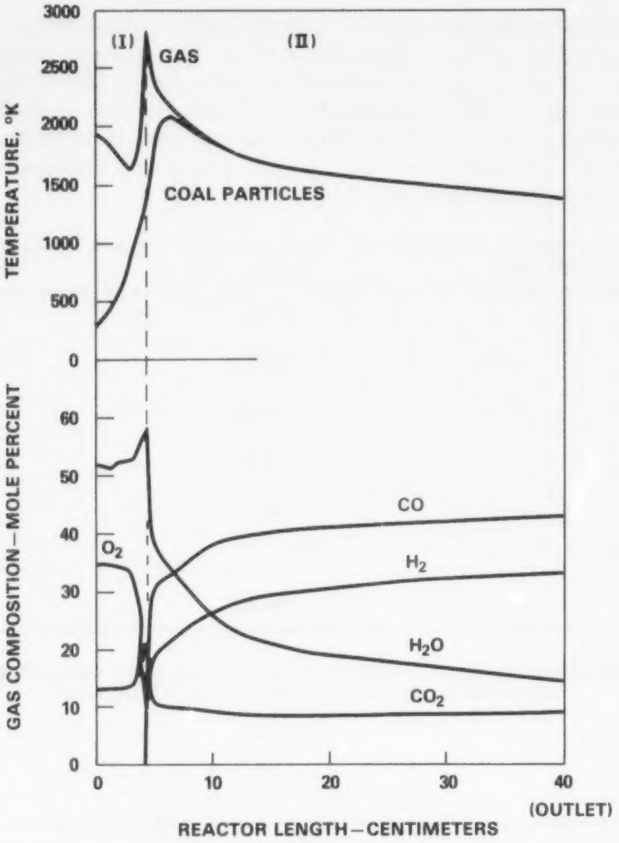

FIGURE 8. TEMPERATURE/COMPOSITION PROFILE ENTRAINED GASIFIER
(P. SMITH, BRIGHAM YOUNG UNIVERSITY)

PROCESS		PHENOL LEVEL, PPM*			
	COAL RANK:	LIGNITE	SUBBITUMINOUS	BITUMINOUS	
			MONTANA	ILLINOIS NO.6	PITTSBURGH NO. 8
LURGI/BRITISH GAS SLAGGING LURGI (WESTFIELD, SCOTLAND)		–	4,400	1,900	2,100
		NORTH DAKOTA	WYOMING		
PETC SYNTHANE (FLUID-BED)		6,600	6,000	2,600	1,700

*NOTE—ABSOLUTE CONCENTRATIONS ARE DEPENDENT ON QUENCH WATER CONTACT/RECYCLE ETC. WHICH DIFFER BETWEEN PROCESSES. TRENDS ARE IMPORTANT.

FIGURE 9. COMPARISON OF CONDENSATE WATER PHENOLIC CONTENT FROM DIFFERENT RANK COALS

Solid and semi-solid sludges and biosludges will result from wastewater treatment. The composition of these potentially biohazardous sludges will be variable. It is likely that the sludges will be rendered non-hazardous by oxidizing them at high temperatures by incineration (direct or fluid bed) or combining them with the coal feedstock or carbonaceous bottoms to be recycled to a high temperature gasifier. The role of wet-air oxidation to detoxify these sludges is under investigation.

ENVIRONMENTAL SETTING

Federal guidelines and standards along with state and local permitting authorities set the effluent specifications. Special site specific conditions and concerns can lead to stringent regulations which could conceivably dictate the degree of treatment and even the requirement for "zero discharge."

REPRESENTATIVE TREATMENT TRAIN

While a universal wastewater treatment train configuration does not exist, a inventory of unit operations are generally available to the different systems proposed for treating the condensate waters associated with low temperature coal conversion processes (Figure 10). Subsequent discussion will be confined to the treatment of low temperature condensate waters, representative of the most difficult to-treat waters, since coal pile runoff and sanitary wastes are susceptible to conventional treatment practice. The major unit operations are arranged with wastewater of intermediate compositions and/or dilution potential being interjected at various points along the treatment train. The sequence of the various steps, in particular, the extraction and stripping operations, may be interchanged:

Oil Separation

As a pretreatment to remove suspended oil, tar, grease and solids (includes settling ponds with skimmers, API separators, contrifuges, etc.). These pretreatments are not highly effective for emulsions, small particles, and substances which possess densities near that of the aqueous phase; thus dissolved air floatation which can remove these materials is sometimes employed as a follow-up pretreatment.

Steam Stripping

Removes volatile material, namely dissolved gases (NH_3, CO_2, H_2S, HCN and COS). Light, low boiling organics may also be removed. Steam requirements may vary from 0.05 to 0.2 lb. steam/lb. wastewater. Means must be provided to facilitate caustic addition to free fixed ammonia, because meeting free ammonia effluent limits in the final effluent is difficult with poorly stripped raw feeds. Process sewer streams typically require steam stripping prior to biotreatment.

Solvent Extraction

Removes gross organics, phenols and polyhydric aromatics, in particular.

Methyl isobutyl ketone (MIBK) and diisopropyl ether (DIPE) are preferred solvents, the MIBK having the broader selectivity for organic material. The requisite solvent recovery step generally involves stripping. When used in conjunction with biological systems solvent extraction tends to dampen fluctuations in organic loadings and potential toxic effects.

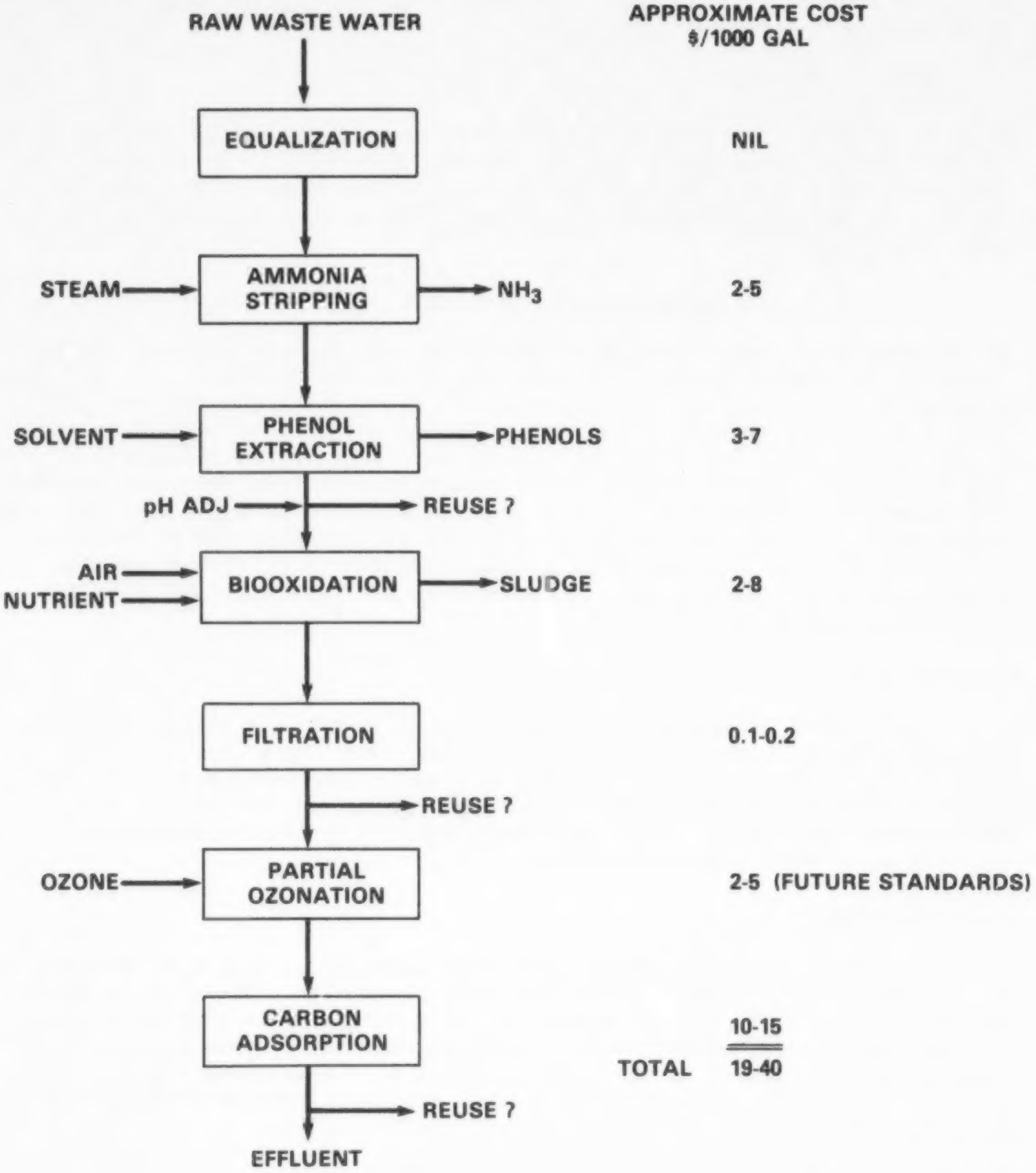
RAW WASTE WATER
APPROXIMATE COST
$/1000 GAL
EQUALIZATION
NIL
STEAM
AMMONIA STRIPPING
NH_3
2-5
SOLVENT
PHENOL EXTRACTION
PHENOLS
3-7
pH ADJ
REUSE ?
AIR
NUTRIENT
BIOOXIDATION
SLUDGE
2-8
FILTRATION
0.1-0.2
REUSE ?
OZONE
PARTIAL OZONATION
2-5 (FUTURE STANDARDS)
CARBON ADSORPTION
10-15
TOTAL
19-40
REUSE ?
EFFLUENT

FIGURE 10. REPRESENTATIVE WASTEWATER TREATMENT TRAIN FOR COAL CONVERSION EFFLUENTS

Biological Treatment

Applicable where effluent discharge and/or reuse of a low biological oxygen demand (BOD) water is contemplated. Activated sludge treatment has a long and successful history of dealing with coking and petroleum refinery wastes which are similar in many respects to coal condensate waters. One of the principal advantages is the forgiving nature of the biological system in its ability to adapt to variable feed composition, provided abrupt changes are not encountered. It is capable of removing all the BOD (by definition) and approximately 75% of the chemical oxygen demand (COD) in the condensate waters. The susceptibility of the biological process to upsets and toxicity effects can be mitigated by introducing powder activated carbon (PAC) to the reactor. This also improves the settlability of the sludge. Polynuclear aromatics, some of which are refractory and collodial in nature, along with heavy metals, may be incorporated with the sludge and must be dealt with during disposal. The thiocynate content of the incoming feed can present difficulties, if a stringent free ammonia discharge standard must be met. The biological degradation of thiocynate releases NH_3 which may require subsequent air stripping and/or biological nitrification/denitrification. The latter step generally requires long residence times, e.g., holding ponds.

Carbon Adsorption

A polishing step to remove low level refractory organics and color bodies and may serve as a safeguard for process upsets. Prefiltration is normally required to preclude fouling of the bed. Pollutants may be leached from the bed immediately after carbon regeneration--recycle may be required.

While this touches on the more prominent conventional processes, there are a large inventory of treatment processes that may be brought to bear for special applications (Figure 11). The treatment of wastewater to discharge quality by such a train is not cheap by municipal standards. Costs are in the range of $20-35/1000 gals. This translates into an expense of 5-10% of projected synfuel selling costs--hardly a barrier to commercialization.

A recent study has shown that, if raw water and an acceptable discharge acceptor (large river or lake) is available to the plant site, e.g., an Eastern location, the most cost effective and preferred approach is to use a once-through water management plan based on PAC-biological treatment and regeneration of the PAC by wet air oxidation, as opposed to water recycle/reuse and/or "zero discharge" alternatives.

AREAS OF CONCERN AND FUTURE RESEARCH

The technology just discussed has assumed the availability of water and steady-state operation. If one considers "zero discharge" and the facility for handling process upsets, the representative treatment train needs some refinement or possible replacement. Before addressing the more stringent requirements imposed by "zero discharge" and unsteady operation, it appears useful to outline areas were perhaps the conventional technology could be improved or at least better understood.

						TREATMENT COST			
			APPLICABILITY				DEPENDENCE ON		
	CONSTITUENT TREATED								
UNIT OPERATION	ORGANIC	INORGANIC	GROSS REMOVAL	POLISHING	BY-PRODUCT RECOVERY	RANGE $/1000 GAL	EFFLUENT QUALITY	EFFLUENT QUANTITY	BASIS FOR RANGE
GRAVITY SEPARATION	✓	–	✓	–	–	0.10–0.20		✓	
STEAM STRIPPING	✓	✓	✓	–	✓	∿10		✓	
SOLVENT EXTRACTION	✓	–	✓	–	✓	∿5		✓	
BIOLOGICAL	✓	–	✓	–	–	10–20	✓		10,000ppm BOD
CARBON ADSORPTION	✓	–	–	✓	–	6–12	✓		2,000ppm COD CARBON REGEN
OZONATION	✓	–	–	✓	–	5	✓		600ppm TOC
PRECIPITATION W/IRON	✓	✓	–	✓	–		✓		
WET-AIR OXIDATION	✓	–	✓	–	–	∿25	✓	✓	
ION EXCHANGE	–	✓	–	✓	✓	0.5–2	✓	✓	
DESALINATION PROCESSES	–	✓	✓	–	✓	5–10		✓	
INCINERATION/GASIFICATION	✓	✓	✓	✓	–		✓	✓	
DEEP-WELL INJECTION	✓	✓	–	–	–			✓	

FIGURE 11. SELECTED WASTEWATER TREATMENT OPTIONS

STATE-OF-THE-ART TREATMENT PROCESSES

Reviewing the characteristics and concerns associated with the major unit operations, several areas of research may be highlighted:

Oil Separation

The use of expendable/regenerable absorption media may be used to scavenge for neutrally bouyant entrained oleophillic materials. Absorbents such as coal, crushed slag, sand, etc., could be employed in a fluid-bed. Much of the multi-ring structured organic material is sparingly water soluble and is in the colloidal state; it appears that clarification and/or filtration enhanced with appropriate flocculation aids and polymer addition could significantly reduce the concentration of these materials.

Steam Stripping

Stripping is preferred for NH_3 concentrations >250 ppm. Subsequent, ammonia recovery is economical via the PHOSAM W or the Chevron process at NH_3 concentrations of 10,000 ppm and flows of 250-500 gpm. The preferred location of the steam stripping unit, before or after the extraction step, if extraction is employed, needs to be determined. Volatile organics are decreased if the stripper is located downstream of the extraction unit; however, residual dissolved solvent may enter the stripping system. The addition of lime to free fixed ammonia and reduce steam requirements also can be used to precipitate heavy metals. The addition of the lime, typically after the stripping of acid gases and free ammonia, increases softening requirements, if intensive reuse and/or concentration of waste brines is planned. A promising alternative under study is to use a liquid cation exchanger to selectively recover ammonia as a by-product and enhance stripping of the acid gases.

Solvent Extraction

As indicated, the preferred sequencing of the steam stripping and solvent extraction is not clearly established. High pH, characteristic of intensive ammonia stripping operations, causes appreciable ionization of phenols and correspondingly leads to lower distribution coefficients, the requirement of higher solvent to water ratios, and ultimately to a more costly process. The most difficult-to-extract component normally dictates the controlling solvent to water ratio. Extraction is capable of removing entrained organics such as polynuclear aromatic micelles. With the proper solvent or combination of solvents, extraction could also be effective at removing the more polar, hydrophillic organics which comprise that significant fraction of the TOC which is not extracted by commercial extraction processes, e.g., DIPE, MIBK, etc., nor by conventional analytical procedures, i.e., methylene chloride. For example, trioctyl phosphine oxide (TOPO), a stronger Lewis base than ketones, has been shown to remove 90% of the COD when used on a representative condensate water. TOPO is costly ($7-8/lb.) and solvent recovery is critical. Concomitant with the development of improved solvents and solvent systems, effective means of solvent regeneration/recovery need to be stressed.

Approximately 70% of the cost for extraction is equipment related, in contrast to stripping where a major portion of the cost is for steam. Extractor costs are nearly proportional to the number of stages. Thus there is incentive for better solvents, improved stage efficiency and an approach to true counter-current operation. One might consider the use of ultrasonics, cavitation, etc., to obtain intimate contact between solvent and solute (especially when a low volume solvent to water ratio is used) and membranes to break the resultant emulsion. The potential role of membranes in solvent recovery may be worth exploring.

Biological Treatment

While biological treatment is effective, it is necessary to pretreat the feed or dilute it to bring the high BOD loadings (phenol in particular) to an acceptable level. With dilution, large volumes of bio-reactors are needed due to high (recycled) influent flows and residence times of several days. Solvent extraction becomes attractive for BOD levels of greater than 2000 ppm. It also reduces difficulties due to foaming. There is incentive for reducing the volume of the bioreactor systems. The use of oxygen enrichment (on-site generated oxygen is available at most coal conversion plants) should be considered to reduce volumes. The use of fluid bed bioreactors is being studied to greatly increase volumetric loadings of biosubstrate with a corresponding decrease in residence time requirements. Oxygen availability becomes controlling in such a system--coupled with enriched air, approximately an order of magnitude decrease in residence time can be achieved. While fluid bed systems require pumping power to recycle the wastewater and maintain the bed, the energy requirements are about one half those associated with aeration for air-activated sludge systems. Because of the reduced residence times, and availability of developed substrate to the process, it is anticipated that fluid bed reactors will be more accommodating to process variability and recover more quickly from process upsets. The potential role of PAC to help mitigate possible upsets in fluid bed biosystems should be investigated. Bioreactor staging can be considered as another means of increasing specific bioactivity and better accommodating process variability. In a single mixed reactor, concentrations are close to effluent concentrations; consequently, reaction rates are low. By approximating plug flow through staging, higher BOD loadings can be effected on the average, along with higher reaction rates. Appropriate real time instrumentation to anticipate toxic effects is desired, in lieu of monitoring completeness of thiocyanate degradation as a lead indicator.

It has been shown that the major fraction of TOC resistant to biological degradation has a molecular weight $>$ 30,000 and likely represents bio-organism wastes. Research at characterizing of and determining techniques for removing these materials is needed. It is quite likely that they are sparingly soluble and enhanced clarification/flocculation techniques could be applicable.

Carbon Adsorption

Because carbon consumption is related directly to the TOC of the water being treated, activated carbon is generally used as a polishing step. The performance of carbon with respect to the high molecular weight organics, touched on above, is uncertain. It has been found that ozonation prior to treatment improves the adsorption efficiency for multi-ring compounds from 50-60% to 90% or better. A major uncertainty exists with respect to carbon regenerability, especially in brackish waters. Acceptable carbon treatment costs are based on the premise of complete regeneration, with secondary loss and make-up of 5%. The actual capacity, effectiveness of regeneration and costs, for activated carbon when used in a polishing mode on condensate water needs to be better established.

PHYSICAL/CHEMICAL OPTIONS

Alternative treatment processes deserve consideration due to the relative high costs associated with the series of five or more process steps that comprise the typical state-of-the-art treatment train. An additional consideration is the concern over system reliability resulting from sequencing several unit operations, especially when a biological step, that is vulnerable to upsets, is in the train.

As previously indicated "zero discharge" considerations can impose an additional and overriding constraint. An end-of-the-pipe approach is to use desalting technology to control the salt content of the effluent to render it suitable for recycle/reuse at the front end of the process. The high quality of the effluent from the representative treatment train should insure the effluent is amenable to conventional desalting (distillation/reverse osmosis) and, depending on the hardness, some softening may be desirable to facilitate high product water recovery and reduce the quantity of brine that requires further concentration/disposal. Cooling towers have been universally used to cost-effectively reject process heat and perform the initial concentration of process wastewaters. Typically, filtered effluent from the activated sludge unit is used as make-up to the tower, although use of DIPE extracted, steam stripped condensate water is contemplated for the ANG dry-ash Lurgi plant at Beulah, North Dakota. Based on petroleum experience, it appears that cooling towers can handle BOD loadings up to 500 ppm in the make-up water. An area of concern, in addition to potential drift and odor difficulties, is the allowable concentration factor before biofouling and corrosion problems become a detriment to the heat exchanger loop. A study is underway to obtain a better handle on these limitations.

Ideally, one desires a single process step that can take the raw wastewater process stream and produce a moderate to good quality stream suitable for reuse and a small highly contaminated stream that can be treated intensively (Figure 12). Solvent extraction (previously discussed), distillation (vapor recompression, in particular), and membrane processes represent candidates for the major separation process, while wet-air oxidation, incineration, gasification, dirty steam generation, etc., could be used to deal with the resultant concentrate and render it acceptable for ultimate disposal. Distillation and membrane processes also can be used to retain the salts in the concentrated stream and, in this respect, are superior to solvent extraction which must be coupled with ion exchange or another desalination process to achieve this end. It should be noted that the product water may concentrate stream will have a very small volume, high unit processing costs can be tolerated. The limitations and tradeoffs associated with the distillation of poor quality wastewaters require better definition. The full integration of these processes with the conversion plant, proper, should be emphasized. Costs are estimated to be in the range of \$6-12/1000 gallons, thus there appears to be adequate leeway for system refinement and optimization to be competitive with a conventional treatment train.

Membranes

The potential application of membrane processes (ultrafiltration and reverse osmosis) to the concentration of raw coal condensate waters is relatively long range. Progress has been made in producing composite membranes from stable substrate polymers such as a porous polysulfone coated with an exceedingly thin film ($\sim$200Å) of salt rejecting membrane, for example a highly crosslinked polyurea. Polyurea membranes exhibit good stability at high and low pH's and in the presence of aromatic solvents. In general, membrane rejection for ammonia is poor and, as a consequence, any membrane concentration process will probably require steam stripping. The rejection of phenols is improved at high pH's (~11); as a consequence, the addition of lime to abet NH_3 stripping will also enhance rejection of ionizable organics. This is in contrast to solvent extraction processes.

The raw condensate water will likely undergo oil separation and filtration (essential, yet negligible cost pretreatments) prior to the reverse osmosis units. The physical configuration of the membrane unit has a bearing on the capability of handling a fouling/dirty feed--dead spots must be avoided to preclude the deposition of material and progressive pluging of the unit. Normally, tubular membranes are used (the influent flowing inside the tubes/tubule bundle) to assure positive flow. Membrane units of this configuration are in commercial applications on cheese whey and latex paints. In addition to the preferred membrane composition, open to question is the degree of concentration that can reliably be effected with a membrane unit--5 to 1 represents a conservative estimate, with 10 or 15 to 1 as probably an upper limit. Very preliminary estimates of membrane separation costs are \$4-8/1000 gallon; thus although the recovery may not be as high as vapor-recompression systems, the lower unit costs could more than compensate the larger volume of concentrate subject to subsequent treatment, e.g., wet-air oxidation. It would seem prudent to support a continuing research effort to advance the application of membranes to condensate waters and solvent recovery (previously mentioned).

Wet-Air Oxidation

Ideally wet-oxidation can convert pollutants to CO_2, N_2 and H_2O by reaction with oxygen at high temperature and pressure. Because of the large flows and expense for pressure vessels and heat exchangers, there is considerable incentive for optimizing and moderating reaction conditions. Only limited research is being directed at these tradeoffs. Costs are proportional to water throughput and advantage can be obtained from the combustion heat associated with high levels of organics. Costs are uncertain, but are expected to be in the range of \$20-30/1000 gallons. Wet-air oxidation require a polishing step to remove dissolved gases and/or hydrophillic organics (generally of a low molecular weight) that could interfere with the specific reuse application.

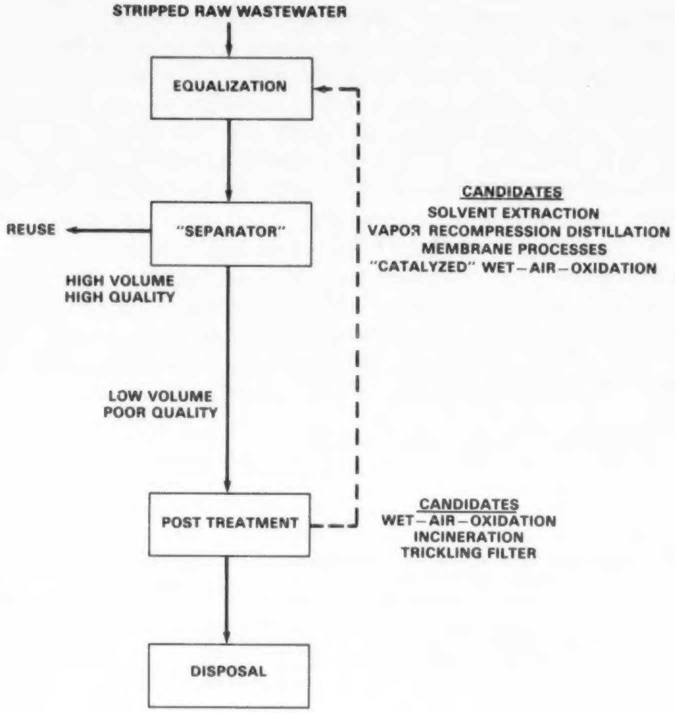
STRIPPED RAW WASTEWATER
EQUALIZATION
REUSE
"SEPARATOR"
HIGH VOLUME
HIGH QUALITY
CANDIDATES
SOLVENT EXTRACTION
VAPOR RECOMPRESSION DISTILLATION
MEMBRANE PROCESSES
"CATALYZED" WET-AIR-OXIDATION
LOW VOLUME
POOR QUALITY
POST TREATMENT
CANDIDATES
WET-AIR-OXIDATION
INCINERATION
TRICKLING FILTER
DISPOSAL

FIGURE 12. PHYSICAL/CHEMICAL OPTION

Distillation

The energy requirements for distillation processes can be greatly reduced by staging (multi-effect evaporators) and/or using vapor-recompression systems. The low quality heat, required for multi-stage evaporation, is readily available on-site and distillation processes might be expected to serve as an effective "bottoming cycle" to the conversion plant. High quality energy is required to run the fan compressor deployed in the vapor-recompression system; this, however, represents a small fraction (approximately 1/50) of the energy required for single stage distillation. Concentration factors as high as 25 have been achieved on raw condensate waters, with pretreatment involving the sequential addition of acid to remove temporary hardness and suppress carbonate scaling and caustic to ionize the phenolic compounds and hold them in the concentrate during the distillation. The distillate may require polishing (activated carbon treatment) for a high quality use such as boiler feed make-up. The concentrate will probably require wet-air oxidation or an equivalent treatment and evaporation to dryness. As the is deserving of continued attention to treat small flows of relatively concentrated streams.

REUSE

A number of water reuse options which avoid release to a surface acceptor are apparently evolving in commercial designs. As previously indicated, many processes are net water consumers; thus there is incentive for closing the "loop." The more prominent reuse options and their advantages and disadvantages are compared in Figure 13. Ideally it is economically desirable to use as poor a quality of water as the reuse application will permit. Many of the recycle systems are merely paper designs and it is not clear that special precaution has been taken to preclude the build-up of trace extractables including organics and corrosion products which may inadvertently react with or precipitate from the recycle loop, thereby impairing the operation and reliability of the system. Many times such difficulties are hard to anticipate. There appears to be room for more systems engineering, tradeoff and optimization at the "tail" of the water use cycle where the waste brine is typically concentrated for disposal. Innovation should be encouraged in this part of the cycle.

OPTION	POTENTIAL ADVANTAGES	POTENTIAL DISADVANTAGES	UNCERTAINTIES
REINJECTION INTO CONVERSION PROCESS	• "ZERO" DISCHARGE • DECREASES WATER USE • CAN CONSERVE SENSIBLE HEAT • LITTLE TREATMENT REQUIRED	• CONCENTRATION STEP MAY BE REQUIRED TO PRESERVE WATER BALANCE • PROCESS CHANGES MAY BE REQUIRED TO ACCOMMODATE	• RELIABILITY AND COST • SOME MATERIALS MAY FAVOR RECYCLE LOOP, MAKING PURGE NECESSARY • NATURE OF SOLID WASTES MAY BE MODIFIED
MAKE-UP FOR COOLING TOWERS	• "ZERO" DISCHARGE • DECREASES WATER USE	• SIGNIFICANT PRETREATMENT MAY BE REQUIRED • MAY NOT BE APPLICABLE ON YEAR-ROUND BASIS	• RELIABILITY AND COST • CONTAMINANTS IN DRIFT MAY PRESENT PROBLEM • CORROSIVE NATURE AND SPARINGLY SOLUBLE CONSTITUENTS MAY PRESENT DIFFICULTY
MAKE-UP FOR FLUE GAS DESULFURIZATION UNIT	• SAME AS ABOVE • COULD IMPROVE FORCED OXIDATION OF SLUDGE	• TRACE METAL PPT MAY ADVERSELY AFFECT LIME REACTIVITY	• TRACE ELEMENTS IN SLUDGE MAY PRESENT PROBLEM
WET-DOWN FOR DUST CONTROL AND IRRIGATION	• "ZERO" DISCHARGE • ASSISTS IN CONTROL OF FUGITIVE EMISSIONS • ABETS REVEGETATION EFFORT	• SIGNIFICANT PRE-TREATMENT REQUIRED • INTRUSION OF TRACE ELEMENTS AND REFRACTORY ORGANICS INTO ECOSYSTEM AND AQUIFERS	• EXTENT OF NATURAL "DETOXIFICATION" OF CONTAMINATED WASTES
BOILER FEEDWATER	• "ZERO" DISCHARGE	• SIGNIFICANT TREATMENT AND DEMINERALIZATION REQUIRED	• COST
FEED FOR SANITARY SYSTEM	• SAVE POTABLE WATER	• TREATMENT REQUIRED TO CONTROL COLOR AND ODOR, ADDITIVES MAY WORK	• COST BENEFIT • COLOR AND ODOR MAY CAUSE OBJECTIONS • EFFECT ON BIOTREATMENT PLANT

FIGURE 13. SELECTED WASTEWATER "REUSE" OPTIONS

CONCLUSION

While existing wastewater treatment technology, which is primarily based on biological oxidation, appears capable of meeting current discharge permit requirements, there is a need for confirmatory operating and performance data on large scale (low temperature) coal conversion facilities that produce and treat large volumes of highly contaminated condensate water. Considerable need and incentive exists for sustaining and expanding the ongoing R&D on state-of-the-art wastewater treatment trains, physical/ chemical alternatives and sludge disposal options. The control and disposal of secondary pollutants which has not been addressed in this presentation should not be overlooked--the problem of salt disposal for "zero discharge systems" remains a concern. Greater emphasis should perhaps be given to system reliability, this aspect assuming greater import as plants get closer to being operative.

ACKNOWLEDGEMENT

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CHARACTERIZATION OF COAL CONVERSION WASTEWATERS USING ON-SITE GC/MS †

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ABSTRACT

This paper discusses a study which was done to characterize a wastewater stream from a coal gasification facility using on-site extraction and GC/MS analysis. The objectives of this program were to:

- Characterize the wastewater organic components primarily for selected Priority Pollutants, Appendix C and Synfuels compounds,

- Investigate the stability of these compounds under refrigeration and ambient storage, and

- Evaluate the destruction of organics by wet oxidation.

Extractable material in the wastewater consisted primarily of phenols and alkylphenols. These compounds accounted for about 98 percent of the total organic mass identified. Several polynuclear aromatic (PNA) compounds were also identified. Deterioration in the composition of the sample was observed over a one month period. This was most evident in the concentration of dimethylphenols which dropped approximately 75 percent during two weeks of refrigerated storage. Ambient sample storage produced a greater decrease in the concentration of phenol but did not appear to affect the alkylphenols or the base/neutral compounds as much as phenol. It is expected that the observed changes in composition would hamper any off-site wastewater treatability studies with water of this type. Treatment of the wastewater by wet oxidation was also evaluated and found to remove greater than 90% of the extractable organics.

INTRODUCTION

The Chapman-Wilputte gasifier at the Holston Army Ammunitions plant in Kingsport, Tennessee, has been the site of several environmental assessment tests. This study deals with an effort to characterize more accurately the aqueous process condensate (separator liquor wastewater) at this facility. Previous studies have shown the Holston process condensate to be similar in composition to the Lurgi process condensate from the Kosovo plant* especially with respect to phenolic compounds.

Lurgi gasification facilities have been proposed for commercial plants in the United States but current operating facilities are not easily accessible. The Holston plant is located in the United States and provides a readily accessible source of coal gasification wastewater for characterization and treatment system development.

Successful treatment of wastewaters requires a good understanding of the composition of the wastewater and the chemistry involved in any decomposition. Previous characterization studies may have been conducted on samples that had deteriorated during shipment and cold storage. Analysis of a deteriorated sample can produce results which do not accurately reflect the composition of the water as it would be fed to a treatment system.

This study included immediate, on-site extractions which were performed in an attempt to minimize any sample deterioration. The on-site Hewlett-Packard Model 5993B gas chromatograph/mass spectrometer (GC/MS) provided immediate analysis of the sample extracts as well as the positive identification of any compound present. It could also identify and track the appearance and/or disappearance of compounds during decomposition.

The main objectives of this program were:

- to provide a more accurate characterization of the aqueous process condensate;
- to investigate sample stability during refrigerated and ambient storage; and
- to investigate the effects of wet oxidation on this wastewater.

PROCESS DESCRIPTION

The Chapman-Wilputte gasification process uses an air-blown, atmospheric pressure gasifier. It gasifies approximately one ton of bituminous coal an hour to produce a fuel gas with average heat content of 150 Btu/scf. The product gas is first quenched then cleaned via direct contact with the process water. The resulting liquor collects in a liquor separator. Here the aqueous layer is decanted from the oils and tars which were removed from the gas stream. The tar layer is recovered for use as a supplemental boiler fuel and the aqueous layer is recirculated through the gas quenching/scrubbing system.

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*Collins, R. V., K. W. Lee, and D. S. Lewis. Comparison of Coal Conversion Wastewaters. EPA 600/9-81-006. Contained in the Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology V, St. Louis, MO, (September, 1980). Radian Corporation, Austin, TX, January, 1981.

Excess water is blown down via an over flow weir to a holding sump. From there, the accumulated water is periodically pumped to a forced evaporator system for ultimate disposal. The brine and tar resulting from the evaporation is returned to the separator. There is no fresh water make up to the system and the net accumulation of water is minimized through the proper operation of the gasification and cleaning systems. Grab samples of the process condensate were collected from the aqueous layer in the separation tank at the point indicated in Figure 1.

PROCEDURES

SAMPLING

Grab samples of the aqueous process condensate were collected from the separator near the off take for the recirculating quench system. The water at this point contained a minimum amount of tar. The pH and temperature of the water were measured at the time of collection.

EXTRACTION

Samples were extracted using a base/neutral-acid extraction procedure. The separator liquor was first basified to pH$\geqslant$12 with NaOH and extracted with methylene chloride followed by diethyl ether to obtain the basic and polynuclear aromatic compounds. It was then acidified to pH $\leq$2 with HCl and extracted as before to obtain the phenolic compounds. The pH adjustment provided enhanced recovery of the basic and acidic compounds and the diethyl ether provided a polar medium for enhanced extraction of phenols. Extracts were concentrated by a factor of ten using a Kuderna-Danish apparatus. Further concentration was not possible due to the large amount of material present in the extracts.

ANALYSIS

Extracts were analyzed using EPA Priority Pollutant conditions* for acid, base/neutral and purgeable componds on a Hewlett-Packard 5993B gas chromatograph/mass spectrometer.

CHARACTERIZATION OF THE AQUEOUS PROCESS CONDENSATE

EXTRACTABLE COMPOUNDS

The base/neutral and acid extracts were analyzed for EPA base/neutral and acid extractable Appendix A Priority Pollutants as well as those compounds listed as Appendix C and Synfuels "priority pollutants". Additional compounds that might occur in coal conversion processes were included based

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*U. S. Environmental Protection Agency. Federal Register 44(233), 69464-69575, 1979.

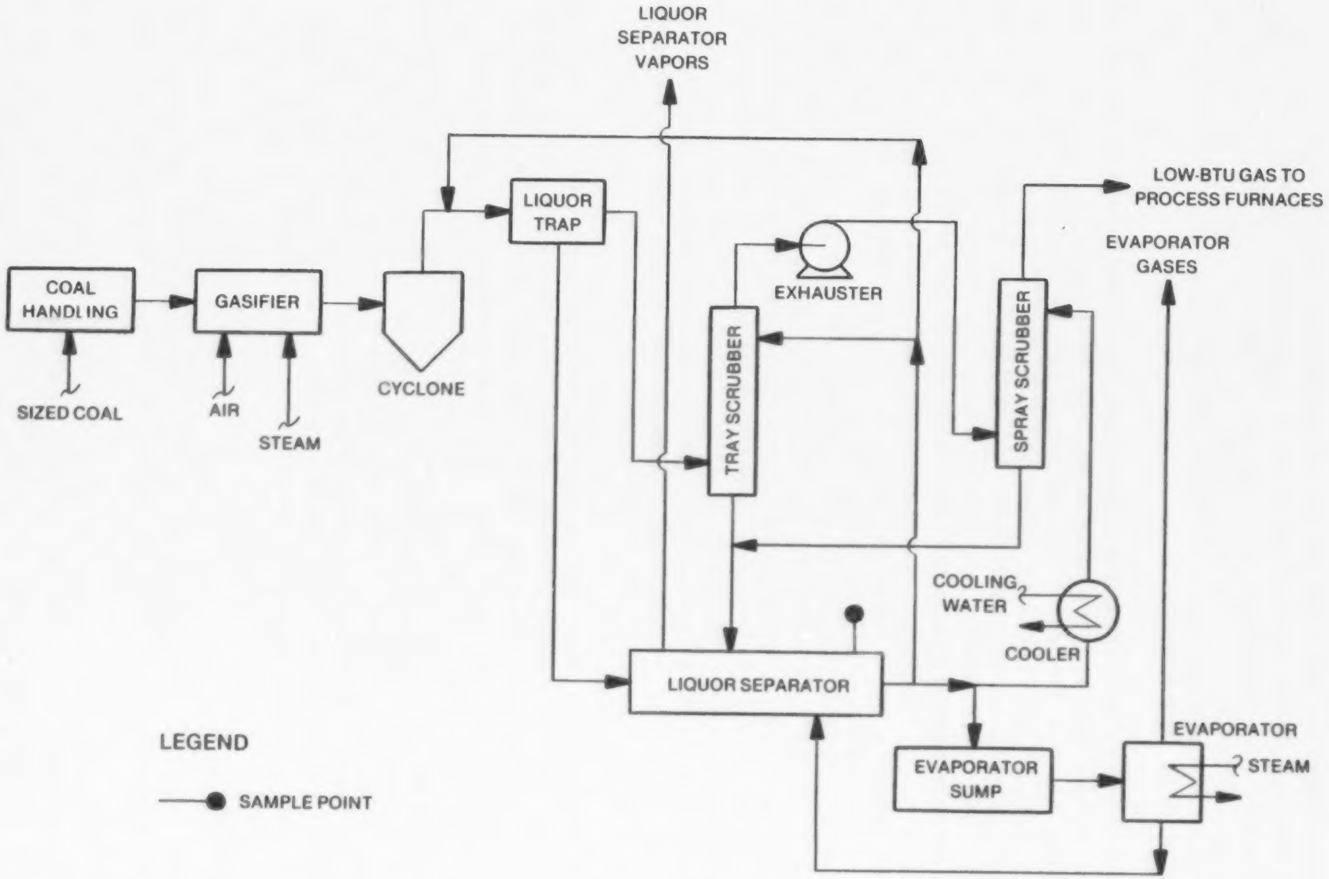
LIQUOR SEPARATOR VAPORS
LOW-BTU GAS TO PROCESS FURNACES
EVAPORATOR GASES
COAL HANDLING
GASIFIER
CYCLONE
LIQUOR TRAP
EXHAUSTER
TRAY SCRUBBER
SPRAY SCRUBBER
SIZED COAL
AIR
STEAM
COOLING WATER
COOLER
LIQUOR SEPARATOR
EVAPORATOR SUMP
EVAPORATOR
STEAM
LEGEND
SAMPLE POINT

Figure 1. Location of water sampling point in process

on their documented behavior in biological oxidation systems* or their known or suspected carcinogenic activity.

Table 1 summarizes the results of the characterization study. The majority of the compounds identified were of a phenolic nature. Phenol, methylphenol, and dimethylphenol account for 98 percent of the total extractable organics. Significant levels of PNA's were also found. The values given represent the average concentration and the range of these values during the six days of monitoring.

The ranges of values indicate that significant variability exists in the data. In an effort to find the source of this variability, a followup study was done using Holston separator liquor which had been collected 24 hours prior to extraction and stored in amber bottles at 4°C since the time of collection. Determinations of instrument variability and extraction variability were made by replicate extractions and replicate analyses of the extracts. Values for representative compounds for instrument variability are given in Table 2. Values for representative compounds for overall (extraction and analysis) variability are listed in Table 3. The instrument variability for total chromatographable organics (TCO) is 1.7 percent while overall variability is 13 percent. This indicates that essentially all of the variability (12.9 percent) is due to extraction for chromatographable organics as a group. This same trend is also seen in the representative compounds presented in the tables except for naphthalene which is close to the detection limit. While the relative standard deviation (1σ) for the overall variability of phenol is only 16 percent, the cresols and naphthalene vary by 47 percent and 34 percent, respectively. These same trends were also observed in the samples which were extracted on-site.

Part of this variability may be due to the complexity of the wastewater sample matrix. The extraction procedure does not produce a clean separation between the base/neutrals (B/N) and the acids (A). Much of the phenolics were extracted into the B/N fraction. The B/N extracts were also analyzed for phenols and the concentrations of phenols found in this fraction added to the values obtained in the acid fraction. The magnitude of this premature extraction is shown in Table 4. The concentrations of phenol show the greatest amount of variability in the base/neutral extract while the concentrations of phenol in the acid extract remain fairly constant. The dimethylphenols, some of the least acidic phenolic compounds identified, demonstrated the greatest amount of extraction into the B/N fraction.

VOLATILE ORGANICS

Volatile species (purgeable halocarbons and aromatics) were also determined in the raw water. These compounds, listed in Table 5, do not show

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*Singer, P. C., F. K. Pfander, J. Chinchilli, A. F. Maciorowski, J. C. Lamb III, and R. Goodman. Assessment of Coal Conversion Wastewaters: Characterization and Preliminary Biotreatability. EPA 600/7-78-181, PB-294 338. University of North Carolina, Department of Environmental Sciences and Engineering, Chapel Hill, NC, September, 1978.

TABLE 1. CHARACTERIZATION DATA FOR EXTRACTABLE SPECIES IN SEPARATOR LIQUOR

Identifications/Compound	Concentration in the Liquor (mg/L)	
	Average	Range
Acid Extractable Compounds		
† Phenol	2400	1900 - 3400
Methylphenols	3200*	1500 - 4700
+ Dimethylphenols (total)	1200	330 - 1900
†‡ 2,4-Dimethylphenol	420	98 - 820
Trimethylphenol	0.82	0.35 - 2.2
Indanol	1.7	< 0.07 - 3.2
1-Naphthol	5.0	3.3 - 8.5
2-Naphthol	6.7	5.4 - 9.2
Resorcinol/Catechol	30	3.6 - 65
Hydroxybenzaldehyde	5.7	< 0.18 - 19
Base/Neutral Extractable Compounds		
† Naphthalene	8.6	1.6 - 17
† Acenaphthylene	3.6	1.2 - < 6
† Fluorene	2.6	0.28 - < 6
† Phenanthrene/Anthracene	2.3	0.7 - < 6
† Fluoranthene	5.7	0.3 - < 9
† Pyrene	5.7	0.4 - < 9
† Bis(2-ethylhexyl)phthalate	12	1.2 - 32[illegible]
✓† Chrysene	0.12	
✓ Benzo(b)fluoranthene	0.10	
✓† Benzo(a)pyrene	0.12	
✓ Pyridine	1.2	
2-Ethylpyridine	18	1.3 - 61
Quinoline	3.1	0.62 - 5.6
✓ 4-Methylquinoline	0.11	
1-Methylnaphthalene	2.3	0.43 - 4.2
2,3-Dimethylnaphthalene	2.3	0.65 - < 4.5
2,6-Dimethylnaphthalene	2.2	< 1.3 - < 3
Indole	12	8 - 14
2-Methylindole	12	2.2 - 16
3-Methylindole	2.4	0.58 - 3.6

† Appendix A Priority Pollutants

* One data point not included in the average was rejected due to extremely high value, but compound was identified 6 of 6 times.

+ Includes 2,4-DMP.

‡ The portion of 2,4-DMP from the B/N fraction was estimated from the amount found in the acid fraction. The value presented here represents the sum of the acid and B/N fraction.
✓ Identified only in one of six samples.

TABLE 2. VARIABILITY IN ANALYSIS

	Average* (mg/L)	% Relative Std. Deviation ($\frac{\sigma}{x}$ x 100)
Phenol	2000 ± 190	9.5 %
Cresol	1200 ± 210	17.5 %
Naphthalene	3.2 ± 1.8**	56.0 %
Total Chromatographable Organics	4200 ± 70	1.7 %

* For three determinations.
**Close to detection limit.

TABLE 3. VARIABILITY IN EXTRACTION AND ANALYSIS

	Average* (mg/L)	% Relative Std. Deviation ($\frac{\sigma}{x}$ x 100)
Phenol	1700 ± 230	16 %
Cresol	800 ± 380	47 %
Naphthalene	3.5 ± 1.2**	34 %
Total Chromatographable Organics	3700 ± 480	13 %

* For three determinations of the combined variability (extraction and analysis).
**Close to detection limit.

TABLE 4. EXTRACTION OF PHENOLIC COMPOUNDS INTO BASE/NEUTRAL EXTRACT

Compound	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6
Phenol (mg/L)						
Acid	1900	2200	1600	1800	1800	1800
B/N	370	590	1800	470	120	100
Total	2300	2800	3400	2300	1900	1900
B/N % of Total	16	21	53	20	6	5
Methylphenols (mg/L)						
Acid	1800	1500	690	1200	900	1100
B/N	2400	3200	30000	2900	580	430
Total	4200	4700	30700	4100	1500	1500
B/N % of Total	57	68	98	71	39	29
Dimethylphenols (mg/L)						
Acid	230	400	44	120	130	81
B/N	1300	1300	1900	1100	220	250
Total	1500	1700	1940	1200	350	330
B/N % of Total	87	76	98	92	63	76

TABLE 5. CHARACTERIZATION DATA FOR VOLATILE ORGANIC COMPOUNDS

	Average* (ug/L)	% Relative Std. Deviation $\left(\frac{\sigma}{x} \times 100\right)$
Benzene	630	12 %
Toluene	420	9 %
Ethylbenzene	48	69 %
Total Xylenes	280	25 %

*For six determinations.

the level of variability seen in the extractable compounds since the additional variability associated with extraction was not introduced.

INVESTIGATION OF SAMPLE STABILITY

The second objective of this program was to determine the effects of refrigeration and ambient storage of the wastewater on the stability of its composition. The refrigerated sample of water was stored in an amber bottle at 4°C for one month, while the ambient sample was stored in an amber bottle at ambient temperatures (up to approximately 35°C) for three weeks. These samples were then extracted and analyzed. The results were then compared to aliquots of the same sample which had been extracted immediately on-site. Figure 2 illustrates how the concentrations of representative compounds decreased with storage. The figure shows that the concentrations of most compounds appear to decrease more during ambient storage than when kept under refrigeration. However, a high relative error associated with the analysis may account for some of the differences observed in concentration between the ambient and refrigerated samples.

Physical changes were also observed in the sample stored under ambient conditions. These include a darkening of the color as well as an increase in the turbidity of the water.

WASTEWATER TREATABILITY BY WET OXIDATION

The third objective of this study was to evaluate the efficiency of removal of organics from process condensate by wet oxidation. The wet oxidation apparatus used to treat the wastewater is shown in Figure 3. Immediately after collection, approximately one liter of the water sample was placed in a stainless steel bomb, heated to 500°F and simultaneously pressurized to 1500 psig with zero air. The bomb remained under these conditions for about 30 minutes. After cooling and then depressurizing, an aliquot of the oxidized water was extracted, analyzed and compared to an aliquot of the unoxidized water sample which had been extracted immediately after sampling.

Table 6 compares the concentrations of each compound determined in the fresh aliquot to those determined in an aliquot of the same sample after wet oxidation. The amount of total extractable organic material is significantly reduced, from 8000 mg/L to approximately 600 mg/L or 8 percent of the original amount. The level of total phenols was reduced to approximately 10 percent of the original concentration. Phenol itself showed the least loss with an 85 percent reduction compared to methylphenols and dimethylphenols which exhibited about a 95 percent reduction in concentration. The less than values represent the detection limit of the instrument for each day of analysis.

Wet oxidation significantly reduced the high concentration of the phenol and alkylated phenols. Previous work by Singer, et al* shows that these

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Singer, P. C., 1978, (op. cit.).

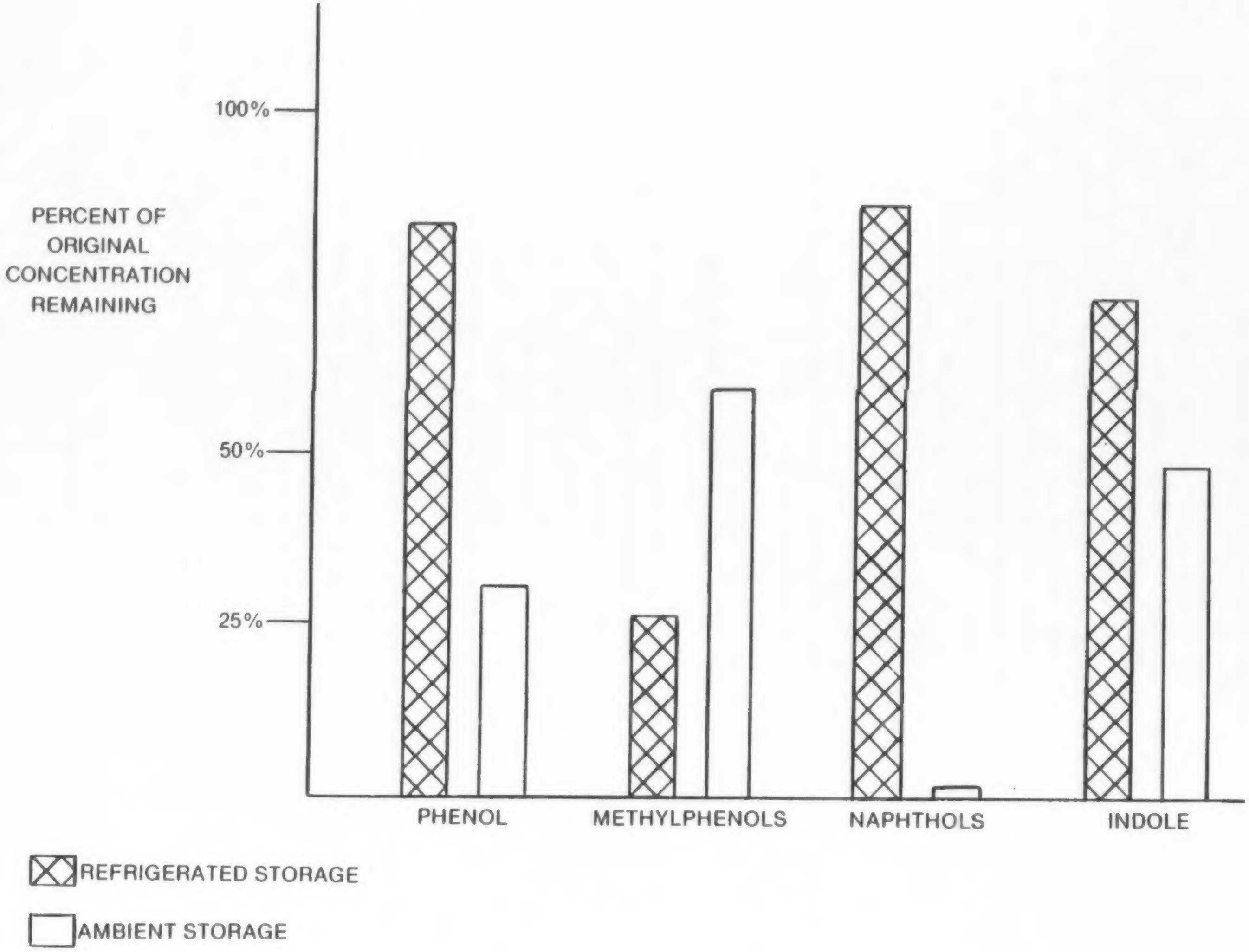
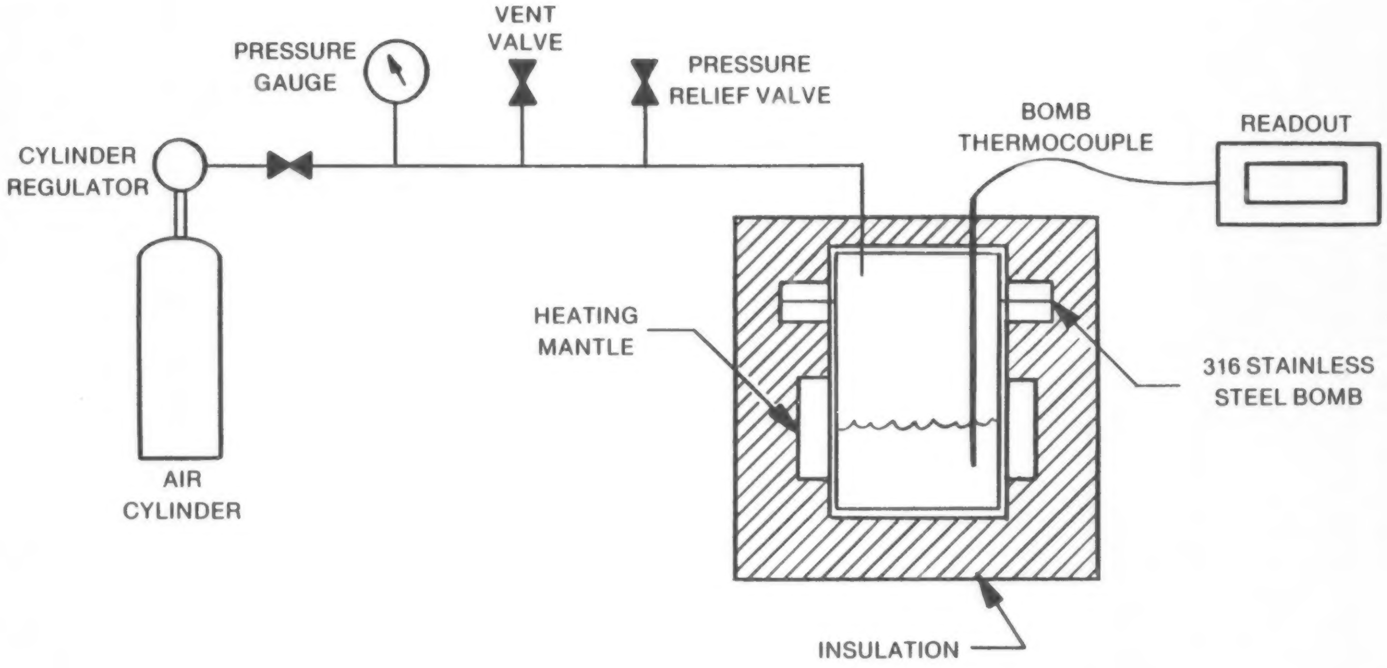


Figure 2. Results of the stability study


PRESSURE
GAUGE
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RELIEF VALVE
CYLINDER
REGULATOR
BOMB
THERMOCOUPLE
READOUT
HEATING
MANTLE
316 STAINLESS
STEEL BOMB
AIR
CYLINDER
INSULATION

Figure 3. Schematic of the wet oxidation apparatus

TABLE 6. EFFICIENCY OF ORGANIC COMPOUND REMOVAL FROM SEPARATOR LIQUOR BY WET OXIDATION

Compound	Resistance to Biodegradation†	Concentration (mg/L) Fresh Sample	After Wet Oxidation	% Removal Efficiency from Control Sample
Total Extractable Organics (as determined by the sum of the total chromatographable organics and the gravimetric residue after evaporation)		7900	600	92 %
Phenol	E	1900	280	85 %
Methylphenols	E	1500	80	95 %
Dimethylphenols	E/R	330	12	96 %
2,4-Dimethylphenol	NR	120	< 2.8	> 98 %
Trimethylphenol	M/R	2.2	< 0.63	> 71 %
Indanol	R	1.2	< 0.27	> 78 %
1-Naphthol	M	4.3	< 0.63	> 85 %
2-Naphthol	E	6.0	< 0.27	> 96 %
Resorcinol/Catechol	E	20	< 2.0	> 90 %
Hydroxybenzaldehyde	E/M	< 0.3	2.2	> 90 %
Naphthalene	E	1.6	< 1	> 38 %
Acenaphthylene	NR	1.5	1.0	33 %
Fluorene	NR	0.49	< 2	NA
Phenanthrene/Anthracene	NR	0.70	< 2	NA
Fluoranthene	NR	0.3	< 3	NA
Pyrene	NR	0.4	< 3	NA
Bis(2-ethylhexyl)phthalate	NR	1.4	0.34	76 %
Chrysene	NR	0.12	< 1	NA
Benzo(b)fluoranthene	NR	0.10	< 1.6	NA
Benzo(a)pyrene	NR	0.12	< 1	NA
Pyridine	R	1.2	< 1	NA
2-Ethylpyridine	R	1.3	< 1.7	NA
Quinoline	E	0.62	< 1.1	NA
4-Methylquinoline	R	0.11	< 1.1	NA
1-Methylnaphthalene	E	0.43	< 1.2	NA
2,3-Dimethylnaphthalene	R	0.65	< 1.6	NA
Indole	M	8.0	< 3.4	> 58 %
3-Methylindole	E	1.4	< 1	> 29 %

† = Reference 2

E = Easily Degraded

M = Moderately Degraded

R = Resistant to Degradation

NR = Biodegradation data not reported

NA = Not Applicable

compounds are also easily treated by bioxidation. However, wet oxidation also has the ability to reduce the levels of organic compounds which are not readily treated by biological systems. Figure 4 illustrates the efficiency of this reduction in the levels of a few representative compounds which are moderately biodegradable and/or resistant to biological treatment. The concentration of 1-naphthol, which is moderately resistant, was reduced by greater than 85 percent; trimethylphenol, which has both resistant and moderately resistant isomers, was reduced by 71 percent and the concentration of indanol, which is resistant to bioxidation, was reduced by greater than 78 percent. In all cases this reduction is greater than 70 percent. This value is outside the limits of the analytical variability discussed previously, indicating definite trends in the removal of organics. Table 6 also indicates the resistance to biodegradation (where available) for each of the other compounds not discussed in this section.

However, despite this efficiency, the overall feasibility of wet oxidation is limited. This is because 1) this technology is still in the developmental stages and 2) there are high costs associated with this process. To date, its usefulness is limited to a few specific applications where there is a need for treatment of highly toxic and/or small volume organic laden streams.

CONCLUSIONS

The following statements summarize the results of this study.

- A loss of sample integrity during sample handling and storage is indicated even when samples are refrigerated.
- Much variability is associated with the complex matrix of this aqueous process condensate. Better separation procedures are required before these samples can be more accurately quantified.
- It is possible to operate a GC/MS system under field conditions.
- About 95 percent (by mass) of the identified compounds are readily biodegradable.
- Wet oxidation reduced the levels of extractable organics by greater than 90 percent.
- Wet oxidation reduced the levels of some compounds which are not readily biodegradable.

RECOMMENDATIONS

The following recommendations, are presented in response to difficulties encountered during sample analysis and data reduction. Since a large source of variability seems to be associated with the extraction of phenols into the

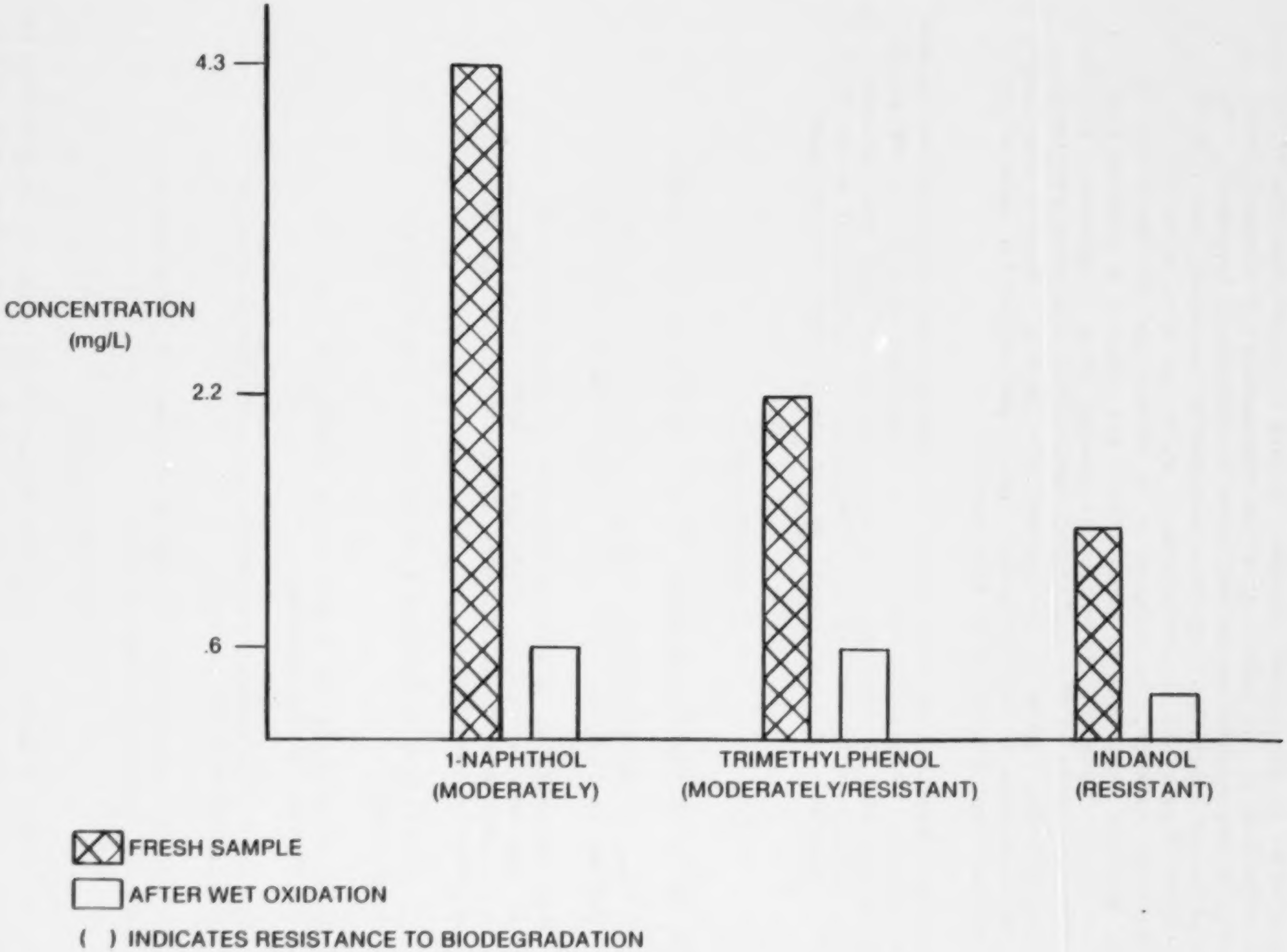

Figure 4. Wet oxidation results for compounds not easily biodegradable

base/neutral fraction, an extraction technique which provides good partitioning of acid and base/neutral compounds is required. This might be achieved by an acid/neutral followed by a basic extraction, then separation of the acid and neutral compounds by liquid chromatography or a less vigorous extraction of base/neutral compounds, using only methylene chloride for the base/neutral compounds, but continuing with a methylene chloride/diethyl ether extraction for the acidic compounds.

Sample analysis could also be facilitated by using a capillary column to provide better chromatographic separation in place of a packed column specified by EPA protocol. Use of the capillary column would allow better speciation of the compounds present.

The need for on-site extraction and GC/MS analysis has not been established. The possiblity of on-site extraction/off-site analysis should also be investigated. The stability of the extracted samples should be evaluated by analysis of the extract immediately after extraction and at predetermined intervals following the extraction to monitor any decrease in one or more compounds. If the stability of extracted samples is adequate to allow transport and storage, the expense of providing on-site analysis could be avoided.

PB83-128298

TREATMENT OF WASTEWATER FROM A FIXED-BED ATMOSPHERIC COAL GASIFIER†

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ABSTRACT

Previous studies using a simulated coal conversion wastewater have demonstrated the feasibility of treating this type of waste by an activated sludge process. Phenol concentrations were reduced to levels below 1 mg/l and the toxicity and mutagenicity of the simulated wastewater were reduced substantially by the biological treatment. This paper will present the results of an evaluation of the biological and subsequent physical-chemical treatability of a real coal conversion wastewater, along with a comparison of the results with those obtained using the simulated wastewater.

Coal gasification wastewater was obtained from a Chapman gasifier at the Holston Army Ammunition Plant in Kingsport, Tennessee. The wastewater was diluted to 25% of full-strength, supplemented with phosphate, and subjected to aerobic biological treatment in a 22.5-liter completely-mixed activated sludge reactor. The reactor was operated at a solids retention time of 20 days and a hydraulic detention time of 10 days. In addition to characterizing the quality of the effluent using various chemical and bioassay procedures, the effluent from the biological reactor was subjected to a series of physical-chemical treatment steps consisting of chemical coagulation, ammonia stripping, ozonation, and activated carbon adsorption. The chemical quality and bioassay characteristics of these various samples will be presented.

INTRODUCTION

Previous research at the University of North Carolina has dealt primarily with an assessment of the biological treatability of a simulated coal conversion wastewater (1,2,3). A 25% dilution of the simulated wastewater was fed to a series of completely-mixed activated sludge reactors, operated at several different solids retention times (sludge ages). The results indicated that TOC, COD, and BOD removal increase with increasing sludge age, and that phenol is essentially completely removed with a sludge age of 5 days. Cresols and xylenols required 10 and 20 days, respectively, for removal to levels below 1 mg/l. Bioassays of the raw and treated quarter-strength simulated wastewater showed that the acute toxicity of the wastewater to fish and to mammalian cells is reduced markedly as a result of the biological treatment and that the extent of the reduction in toxicity increases with increasing sludge age. Additionally, at the concentrations tested, biological treatment reduces the mutagenic activity associated with the raw simulated wastewater to undetectable levels.

BIOLOGICAL TREATMENT OF HOLSTON WASTEWATER

More recently, we were able to obtain a real coal gasification wastewater from the Holston Army Ammunition Plant in Kingsport, Tennessee. The Holston facility has a fixed-bed, atmospheric Chapman gasifier which produces a low Btu gas which is used as fuel for process heaters. The wastewater sample was collected by R. Collins of the Radian Corporation (4) from the separator liquor tank which receives process condensate and condensed tars and oils from the gas-quenching and scrubbing steps at the Holston facility. Separation of tars and oils was reasonably good as the aqueous wastewater sample was relatively free of particulate material. The wastewater was sealed in 55-gallon drums to preserve its chemical integrity and shipped to our laboratories in Chapel Hill. Upon receipt of the drums, a sample of the virgin wastewater was collected, under an argon atmosphere, for chemical analysis and for various aquatic and health effects bioassays. The remaining contents of the drum were re-sealed and stored under an argon atmosphere in order to avoid exposure of the wastewater to oxygen and to minimize the loss of volatile constituents of the wastewater.

Table 1 presents the chemical characteristics of the virgin Holston wastewater as it was received. Two different shipments were received, and the characteristics of each of the batches are shown. Batch 2, the second shipment, is stronger than Batch 1, particularly with respect to COD and ammonia. The composition of the simulated coal conversion wastewater used in our earlier studies (1, 2, 3) is shown for comparison. The concentrations of phenols, TOC, and COD in the simulated wastewater are comparable to those in Batch 1 of the Holston wastewater; the ammonia concentration is appreciably lower.

TABLE 1. CHARACTERISTICS OF VIRGIN HOLSTON WASTEWATER

	Concentration, mg/1*		
Parameter	Batch 1	Batch 2	Simulated Coal Conversion Wastewater
TOC	5,450	7,090	4,640
COD	14,800	25,000	14,300
BOD_5	8,000	-	7,070
4-AAP Phenols	2,000	2,320	2,240
CN^-	4.1	21.7	-
SCN^-	600	950	-
NH_3, as N	3,770	7,260	1,000
pH	8.0	8.04	7.1

*Except pH

Batch 1 of the raw Holston wastewater was also analyzed for selected trace metals and polynuclear aromatic hydrocarbons (PAH). These analyses were performed on samples taken several weeks after the drum was first opened so that a significant amount of suspended material was found in the aged wastewater. Accordingly, both the aqueous and solid phases were analyzed. Table 2 shows the concentrations of these selected priority pollutants in the raw wastewater. With the exception of zinc which was present at a concentration of 1.3 mg/l, the trace metals were found at concentrations less than 0.2 mg/l. The concentrations of each of the PAH were less than 0.1 mg/l; the high value reported for pyrene is questionable.

TABLE 2. CONCENTRATIONS OF TRACE METALS AND POLYNUCLEAR AROMATIC HYDROCARBONS IN RAW HOLSTON WASTEWATER*

	Concentrations, mg/l		
	Dissolved	Suspended	Total
Metals			
Cr	0.032	0.016	0.048
Cu	0.056	0.144	0.200
Mn	0.020	0.104	0.124
Zn	0.828	0.496	1.324
Pb	0.080	0.056	0.136
PAH			
Naphthalene	0.024	<0.036	0.024-0.060
Fluorene	0.008	<0.016	0.008-0.024
Phenanthrene	<0.012	<0.048	< 0.060
Anthracene	0.048	<0.044	0.048-0.092
Pyrene	0.528**	<0.056	0.528-0.584**

* Batch 1

** Questionable

Table 3 shows the toxicity of Batch 1 of the virgin Holston wastewater to Daphnia, fathead minnows, and the Chinese hamster ovary (CHO) mammalian cell system. The toxicities are relatively comparable for each of the bioassay systems, with LC50s on the order of 0.1%, i.e. 0.1 ml of wastewater diluted in 100 ml of clean water will cause 50% lethality of each of the bioassay indicators. Again, for purposes of comparison, the toxicity of the full-strength simulated wastewater is also shown in Table 3. From a toxicity standpoint, the Holston wastewater is approximately four to five times stronger (more toxic) than the simulated wastewater with which we previously worked.

TABLE 3. TOXICITY OF VIRGIN HOLSTON WASTEWATER

A. Virgin Holston Wastewater*

	LC50, %			
Aquatic Toxicity	24-hr.	48-hr.	72-hr.	96-hr.
Daphnia	0.28	0.11	--	--
Fathead Minnow	0.11	0.10	0.09	0.09

Mammalian Cytotoxicity	LC50, %
CHO Monoclonal Assay	0.12

B. Simulated Coal Conversion Wastewater

	LC50, %			
Aquatic Toxicity	24-hr.	48-hr.	72-hr.	96-hr.
Daphnia	0.41	0.21	0.19	<0.11
Fathead Minnow	0.5	0.5	0.49	0.49

Mammalian Cytotoxicity	LC50, %
CHO Monoclonal Assay	0.48

*Batch 1

The wastewater was diluted to 25% of full-strength, supplemented with phosphate, and subjected to aerobic biological treatment in a 22.5-liter completely-mixed activated sludge reactor. The reactor was operated at a 20-day solids residence time and a 10-day hydraulic retention time. No other pre-treatment was provided. Table 4 shows the chemical quality of the reactor effluent compared to the diluted raw feed. Both batches of wastewater appear to be treated relatively effectively, with TOC removals of approximately 66% and 62% for batches 1 and 2, respectively, and COD removal averaging 63% and 62%, respectively. The average effluent TOCs and CODs are respectively 510 and 1650 mg/l for batch 1 and 629 and 2145 mg/l for batch 2. The differences presumably are due to the fact that batch 2 is appreciably stronger than batch 1.

In both cases, substantial removal of phenols (as measured by the 4-aminoantipyrene wet chemical procedure) occurred. The residual concentration of phenols was frequently below 1 mg/l. HPLC analysis showed that phenol itself was usually on the order of 0.1-0.2 mg/l in the reactor effluent.

TABLE 4. QUALITY OF BIOLOGICALLY-TREATED* HOLSTON WASTEWATER

	Concentration, mg/l**					
	Batch 1		Batch 2		Simulated Coal Conversion Wastewater*	
Parameter	Reactor Influent	Reactor Effluent	Reactor Influent	Reactor Effluent	Reactor Influent	Reactor Effluent
TOC	1510	510 (±81)	2000	629 (±67)	1410	204 (±51)
COD	4490	1650 (±209)	5580	2145 (±470)	3326	511 (±121)
BOD_5	1700	26	--	--	1770	22
4-AAP Phenols	526	1.2-3.3	498	0.2-3.6	560	0.14-2.6
CN^-	1.0	1.0	--	--	--	--
SCN^-	173	162-193	253	443-483	--	--
NH_3, as N	882	874	1810	1890	252	212
pH	7.48	7.45	7.0	7.0	7.1	6.9

*Activated sludge; 10-day HRT, 20-day SRT
**Except pH

No biological nitrification was observed, with effluent ammonia concentrations being similar to the influent ammonia concentration. No thiocyanate removal was apparent, although our results indicate an apparent increase in SCN^- for batch 2. Such a production of SCN^- has not been reported previously, yet we have measured this increase consistently, and have verified our analytical results using step addition procedures. Thiocyanate was measured using the spectrophotometric dithiocyanatopyridine chloroform extraction procedure (5).

Table 4 also shows the quality of the biologically-treated simulated coal conversion wastewater under parallel treatment conditions, i.e. diluted to 25% of full-strength and treated by an activated sludge system with a solids retention time of 20 days and a hydraulic retention time of 10 days. Treatment of the simulated wastewater was more effective, providing an 86% reduction in TOC and an 85% reduction in COD. The effluent TOC and COD concentrations are approximately 1/2 to 1/3 of those in the biologically-treated Holston effluent.

Table 5 shows the toxicity of the raw and biologically-treated Holston wastewater. The "raw" LC50s refer to the 25% diluted Holston wastewater corresponding to the influent to the biological reactors. It is apparent that there is a significant reduction in aquatic toxicity to the Daphnia and fathead minnows, and in the CHO mammalian cytotoxicity; 5 to 15-fold reductions in toxicity result from the biological treatment of the diluted Holston wastewater, using these assay systems. Because of the variability in effluent quality and in order to provide toxicity data for both batches of the raw wastewater, the bioassays were performed several times, as indicated by the dates in Table 5. (The reactor feed was switched from batch 1 to batch 2 in early April, 1980.) The LC50 values seem to be fairly consistent irrespective of this variability in gross chemical quality.

A comparison between the toxicity of the biologically-treated Holston wastewater and the biologically-treated simulated coal conversion wastewater (see Table 5) shows that the Holston effluent is appreciably more toxic to the three bioassay systems tested. Hence, despite the effectiveness of biological treatment in removing TOC and COD and in reducing the toxicity of the Holston wastewater, the biologically-treated effluent is still of unacceptable quality for discharge to the aquatic environment. The residual TOC and COD are still appreciable, as are the NH_3 and SCN^- concentrations. The toxicity of the effluent is also still substantial, suggesting that additional, i.e. post-biological, treatment is appropriate.

A 25% dilution of the virgin Holston wastewater was assayed for mutagenicity using the Ames test. Preliminary screening experiments showed that TA98 (a strain of Salmonella which tests for frameshift mutagenic activity) to be the most sensitive strain for this wastewater. With metabolic activation (the incorporation of the S-9 rat liver homogenate into the test system), TA98 gave a positive mutagenic response at all sample volumes tested up to 2.5 ml. The highest reversion ratio of 3.4 occurred for 1.5 ml of the wastewater sample.

TABLE 5. TOXICITY OF RAW* AND BIOLOGICALLY-TREATED** HOLSTON WASTEWATER

A. Holston Wastewater

AQUATIC TOXICITY

		LC50, %			
Daphnia	Date	24-hr.	48-hr.	72-hr.	96-hr.
Influent	8/26/80	1.12	0.44	--	--
Influent	6/23/81	1.8	0.76	0.53	0.49
Effluent	10/1/80	6.5	4.6	3.9	--
Effluent	10/27/80	4.5	4.1	3.9	--
Effluent	2/16/81	5.6	3.5	3.2	--
Effluent	6/29/81	4.8	3.3	2.5	--
Fathead Minnow					
Influent	8/12/80	0.44	0.40	0.38	0.38
Influent	5/15/81	1.1	1.0	1.0	1.0
Effluent	10/1/80	11	6.8	5.7	5.2
Effluent	10/15/80	9.6	5.9	4.9	--

MAMMALIAN CYTOTOXICITY

CHO Monoclonal Assay	Date	LC50, %
Influent	8/26/80	0.48
Influent	6/23/81	0.52
Effluent	9/26/80	4.90
Effluent	6/28/81	3.64
Effluent	7/14/81	7.01

B. Simulated Coal Conversion Wastewater

AQUATIC TOXICITY

	LC50, %			
Daphnia	24-hr.	48-hr.	72-hr.	96-hr.
Influent	1.65	0.85	0.7	<0.42
Effluent	57	49	38	--
Fathead Minnow				
Influent	2.0	2.0	2.0	1.9
Effluent	Ind.***	Ind.***	Ind.***	Ind.***

MAMMALIAN CYTOTOXICITY

CHO Monoclonal Assay	LC50, %
Influent	1.9
Effluent	15.7

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*25% diluted Holston Wastewater

**10-day HRT, 20-day SRT activated sludge system

***Greater than 50% of the test organisms survived at concentrations up to 50% of the effluent.

Following biological treatment, no frameshift mutagenic activity, with or without metabolic activation, was found at sample volumes up to 2.0 ml using tester strains TA98 and TA1537. Additionally, no base-pair substitution mutagenic activity, using tester strain TA100 with or without metabolic activation, was found at sample volumes up to 2.0 ml of the treated wastewater. Apparently, mutagenic activity in the Holston wastewater was reduced to undetectable levels by biological treatment.

TABLE 6. MOLECULAR WEIGHT DISTRIBUTION OF RESIDUAL ORGANIC CARBON IN FILTERED ACTIVATED SLUDGE EFFLUENT

Molecular Weight	TOC, mg/l
<500	390
500 to 30,00	70
>30,000	200
TOTAL	660

It is also worth noting that the filtered (0.45 μm) effluent following biological treatment contains a significant amount of high molecular weight organic material as shown in Table 6. The molecular weight distribution was measured by ultrafiltration techniques, using two different membranes with nominal molecular weight cut-offs of 500 and 30,000. Of the 660 mg/l of TOC, approximately 30% or 200 mg/l (on a carbon basis) consisted of organics with a molecular weight greater than 30,000. Sixty percent, or 390 mg/l, of the TOC consisted of organics of molecular weight less than 500. The remainder of the TOC consisted of compounds with a molecular weight in the 500-30,000 range. The fact that approximately 40% of the residual TOC following activated sludge biological treatment is comprised of compounds with a molecular weight greater than 500 implies that the residual TOC may cause problems if the biologically-treated effluent is to be recycled for use in a cooling tower. It is conceivable that these high molecular weight compounds will tend to adsorb to heat transfer surfaces in the tower, thereby fouling the tower and interfering with its operation. The amenability of this high molecular weight organic material to various post-biological treatment processes should be examined.

POST-TREATMENT OF BIOLOGICALLY-TREATED HOLSTON WASTEWATER

Filtered effluent from the biological reactors treating diluted Holston wastewater was subjected to a variety of physical-chemical treatment steps consisting of chemical coagulation and precipitation, ozonation, activated carbon adsorption, and ammonia stripping. The effectiveness of these post-biological treatment processes was assessed through measurements of TOC, COD, NH_3, SCN^-, and residual Daphnia and CHO toxicity.

Table 7 shows the results of coagulation and precipitation experiments on the filtered biologically-treated Holston wastewater. Alum (aluminum sulfate) and ferric chloride are standard water supply and wastewater treatment coagulants and have been shown (6) to effectively remove high molecular weight humic substances from water. Nevertheless, the application of these coagulants, even at extreme doses of up to 500 mg/l, resulted in no apparent floc formation. The chemicals were added to the wastewater, and the water was rapid-mixed to disperse the chemical, slow-mixed to allow for flocculation, and allowed to stand quiescently to provide for settling of any floc or precipitate. The fact that aluminum hydroxide or ferric hydroxide wasn't produced suggests that a substantial concentration of metal-complexing organics are still present in the biologically-treated wastewater.

TABLE 7. COAGULATION OF BIOLOGICALLY-TREATED* HOLSTON WASTEWATER

ALUM

0-500 mg/l at pH 6.5 - no floc formed, no precipitation

FERRIC CHLORIDE

0-500 mg/l at pH 6.0 and pH 8.0 - no floc formed, no precipitation

LIME

Dose, mg/l	pH	TOC, mg/l
0	7.0	640
720	8.5	475
2640	9.3	460
3360	9.6	455
5280	11.6	450

H_2SO_4

0	6.9	600
6.5	3.0	570
10	2.5	480
25	2.0	425
60	1.5	420

BETZ 1190 CATIONIC POLYMER

Dose, mg/l	TOC, mg/l
0	640
200	460
400	410
1000	500
5000	1260

*Filtered activated sludge effluent, 10-day HRT, 20-day SRT

The addition of lime (CaO) raised the pH of the water and, after allowing for settling, resulted in the removal of some of the TOC. Approximately 25% of the TOC was removed by the addition of 720 mg/l of lime which raised the pH to 8.5. Little improvement was achieved with higher doses of lime.

Sulfuric acid caused precipitation of some of the residual organics by decreasing the pH of the wastewater. High molecular weight humic substances tend to precipitate under such acidic conditions. Approximately 30% of the TOC was removed when the pH was reduced to 2.0. Little precipitation of TOC was obtained until the pH of the water was decreased to below pH 3.

The addition of a cationic polyelectrolyte, BETZ 1190, a high charge density, relatively moderate molecular weight polymer, brought about some coagulation of TOC, but again at rather substantial doses. Edzwald (7) has shown that such cationic polymers are effective coagulants of high molecular weight humic substances. The optimal dosage range appeared to be between 200 and 1000 mg/l, with 35% removal of TOC occurring at a dose of 400 mg/l of the polymer. Apparently, little improvement in the quality of the wastewater can be obtained through coagulation or acid or base treatment, even at very high chemical doses.

Table 8 presents the results of an experiment in which the biologically-treated wastewater was treated further in an ozone contact column. A mixture of ozone and oxygen was bubbled through a sample of wastewater, and aliquots were removed at various times and analyzed. The pH decreased substantially during the course of ozonation, presumably due to the conversion of many of the organic impurities to organic acids and CO_2. Thiocyanate was oxidized almost completely by the ozone. Total organic carbon decreased as a result of ozonation, while the COD was decreased to an even greater degree. The relative decreases in TOC and COD suggest that many of the organic compounds were converted to organic acids and aldehydes in which the organic carbon is in a higher oxidation state than in the parent compound, while only a portion of the organic compounds were oxidized completely to CO_2. The ozone consumption, which was calculated by measuring the difference between the applied ozone in the feed gas and the ozone concentration in the off-gas, is relatively small compared to the change in COD and SCN^- concentrations, suggesting that some of the organics were removed by the application of ozone. The initial removal of NH_3 was probably through air-stripping; further ammonia removal was inhibited as a result of the acidic conditions (low pH) which were generated.

Table 9 shows the results of treating filtered biologically-treated Holston wastewater with activated carbon. Pulverized Nuchar WV-G (Westvaco Chemical Co) was used as the adsorbent. The studies were carried out as batch equilibrium experiments in which various doses of carbon were added to the wastewater, and the suspension was mixed for 4 hours to reach equilibrium. Upon equilibration, the activated carbon was removed by centrifugation and filtration, and the residual TOC was measured. Table 9 shows that the extent of TOC removal increased with increasing doses of

TABLE 8. OZONATION OF BIOLOGICALLY-TREATED* HOLSTON WASTEWATER

Ozonation Time min.	Applied Ozone Dose mg/l	Ozone Consumption mg/l	pH	TOC mg/l	COD mg/l	SCN^- mg/l	NH_3 mg/l
0	0	0	6.77	645	2777	428	2608
10	455	450	3.36	566	1801	106	1904
30	1365	910	2.65	520	1431	18	1890
60	2730	1140	2.59	491	1299	11	1820

*Activated sludge, 10-day HRT, 20-day SRT

TABLE 9. ADSORPTION OF BIOLOGICALLY-TREATED* HOLSTON WASTEWATER

Activated Carbon** Dose mg/l	TOC mg/l	COD mg/l	BOD mg/l	Daphnia Toxicity LC50, %		
				24-hr	48-hr	96-hr
0	662	1480	48	5.6	3.5	3.2
800	490	1030	10	-	-	-
1000	440	-	-	-	-	-
1800	380	-	-	-	-	-
2000	354	684	8	5.6	4.5	2.7
3500	283	-	-	-	-	-

*Filtered activated sludge effluent, 10-day HRT, 20-day SRT
**Powdered Westvaco Nuchar WV-G activated carbon

activated carbon and that approximately 50% of the TOC was removed with an activated carbon dose of 2000 mg/l. However, Table 9 also shows that despite the TOC and COD removals achieved by activated carbon adsorption, such treatment had little impact on the toxicity of the wastewater to Daphnia. The LC50s of the carbon-treated samples are essentially the same as those of the biologically-treated effluent with no carbon treatment. This may be a result of the high ammonia concentration of the samples, i.e. the toxicity of the treated wastewater may be due to the approximately 2000 mg/l of ammonia-nitrogen which is still in the wastewater even after the activated sludge and activated carbon treatment.

In order to test this hypothesis, samples of the biologically-treated Holston wastewater were treated with NaOH to raise their pH to approximately 11, air-stripped to release NH_3, neutralized to pH 7 with HCl, and subsequently treated with activated carbon as described above. Table 10 shows that while biological treatment of the diluted Holston wastewater reduced its toxicity to Daphnia and CHO cells by factors of approximately 3 and 13, respectively, reducing the ammonia concentration from 2000 to 110 mg/l (a 95% reduction) resulted in an additional 3- to 6-fold reduction in toxicity.

The reason for the apparent increase in TOC which accompanied the ammonia-stripping step is not known; it may have been due to (a) absorption of organics from the laboratory air that was used to strip the ammonia, although an activated carbon plug was used in the air line to trap any organic contaminants in the air, or (b) to the hydrolysis of some of the high molecular weight residual organics at the elevated pH which makes the organic carbon more amenable to detection by the analytical procedure used to measure TOC. The latter involves a high temperature (950°C) combustion of the organic carbon by oxygen, and measurement of the CO_2 released. Some of the high molecular weight organic carbon in the sample prior to ammonia-stripping may not have been oxidized completely to CO_2 and therefore may have escaped detection.

Table 10 shows that subsequent treatment of the ammonia-stripped biologically-treated Holston wastewater with 500 and 3600 mg/l of activated carbon reduced the TOC by 23% and 53%, respectively, but had no effect on the toxicity of the wastewater to Daphnia. However, the toxicity of the treated wastewater to the CHO cells was reduced to such a degree by activated carbon that more than 50% of the cells survived at all of the wastewater concentrations tested. While these activated carbon doses are relatively extreme, they do illustrate the impact of additional TOC removal on the toxicity of the wastewater.

In view of the reduction in toxicity resulting from ammonia stripping and the improvement in the gross chemical quality of the wastewater following ozonation (see Table 8), filtered biologically-treated wastewater was ammonia-stripped in the same manner as discussed above, and then subjected to ozonation. In this case, the ammonia-stripped wastewater was buffered with respect to pH in order to promote broad-based non-selective oxidation of the residual organics (8). Table 11 shows analytical results parallel to those shown in Table 8: substantial reduction of COD, some removal of TOC, essentially complete elimination of thiocyanate, and no oxidation of the residual ammonia. It appears, however, that cyanide is produced from the oxidation of thiocyanate and, while some of the cyanide is oxidized further by ozone, a significant concentration of cyanide remains in solution even after 60 minutes of ozonation. Correspondingly, the ozonated samples are more toxic to Daphnia and to the microbial seed used in the BOD measurements. In the former case, a quantitative determination of the 24-hr. LC-50 could not be made but it was observed that the 24-hr. LC-50 for the ozonated samples was less than 5% compared to a 24-hr. LC-50 of more than 15% for the ammonia-stripped, biologically-treated wastewater prior to ozonation. In the latter case, the BOD could not be measured using more than a 6% dilution of the wastewater; dilutions greater than 6% were toxic to the microbial seed. While some thiocyanate ozonation studies have already been conducted (9), additional studies are required to determine the relative oxidation kinetics of SCN^- and CN^- and to ascertain whether the observed increase in toxicity following ozonation is due to the generation of cyanide or to other toxic products of the ozonation reaction.

TABLE 10. ADSORPTION OF AMMONIA-STRIPPED BIOLOGICALLY-TREATED HOLSTON WASTEWATER

Sample	TOC mg/l	NH_3 mg/l as N	Daphnia Toxicity LC50, %				CHO Cytotoxicity LC50, %
			24-hr	48-hr	72-hr	96-hr	
Holston Feed (25% strength)	1800	1970	1.8	0.76	0.53	0.49	0.52
Biologically-treated Effluent	600	1950	4.2	1.9	1.5	1.45	7.01
NH_3-stripped Effluent	705	110	17.3	11.8	8.3	8.3	19.4
Activated Carbon-treated NH_3-stripped Effluent							
500 mg/l AC*	540	110	18.8	11.3	10	7.7	Indet**
3600 mg/l AC*	330	110	23	11.8	8.4	7.5	Indet***

*Powdered Westvaco WV-G activated carbon
**Greater than 50% survival at concentrations up to 45%
***Greater than 50% survival at concentrations up to 75%

TABLE 11. RESULTS OF OZONATION STUDIES ON AMMONIA-STRIPPED, BIOLOGICALLY-TREATED HOLSTON WASTEWATER

Parameter	Time of Ozonation, min. 0	20	60
Ozone dose, mg/l	0	900	2700
Ozone consumption, mg/l	0	845	1505
pH	7.10	6.68	6.60
TOC, mg/l	803	744	676
COD, mg/l	2503	1798	1499
BOD, mg/l	115	45*	65*
NH_3, mg/l as N	146	147	153
NO_3^-, mg/l as N	8.0	4.6	10.0
SCN^-, mg/l	607	87	5
CN^-, mg/l	3.3	152	128
Daphnia Toxicity 24-hr LC50, %	>15	< 5	< 5

* Toxic at 6% concentration

SOLVENT-EXTRACTION OF HOLSTON WASTEWATER

In order to evaluate the impact of solvent-extraction of phenols on the biological treatability of the Holston wastewater, a large volume of the virgin Holston wastewater (i.e. a fresh sample from a newly-opened barrel of the wastewater) was extracted with n-butyl acetate. Three extractions, with a solvent-wastewater ratio of 1 to 10, were employed, and the residual butyl acetate in the aqueous phase was eliminated by air-stripping. The pH of the wastewater was raised to approximately 11 with NaOH and the sample was air-stripped to release NH_3. After re-adjustment of the pH to 7 with HCl, the wastewater was supplemented with phosphate and fed without any dilution to an activated sludge reactor operated at a 20-day sludge age and a 10-day hydraulic residence time.

Table 12 gives the results available to date. The solvent-extraction step reduced the concentration of phenols to 8.0 mg/l and resulted in TOC and COD removals of 68% and 67%, respectively. These removals were accompanied by a 6 to 7-fold reduction in Daphnia and CHO toxicity. Ammonia-stripping of the solvent-extracted wastewater to a level of 84 mg/l of ammonia resulted in an additional 6-fold reduction in toxicity to Daphnia. (Again, it should be noted that both TOC and COD appear to have increased as a result of pH adjustment and ammonia-stripping. Hydrolysis of high molecular weight organics or absorption of organics from the laboratory air are, again, possible explanations for this apparent increase.) The results of the biological treatment studies are not available at the time of this writing.

TABLE 12. RESULTS OF SOLVENT-EXTRACTION STUDIES

Parameter	Virgin Holston Wastewater*	Solvent-Extracted Holston Wastewater**	NH_3-stripped,*** Solvent-Extracted Wastewater
TOC, mg/l	7490	2390	2860
COD, mg/l	24,500	8200	10,100
Phenols, mg/l	2200	8.0	-
NH_3, mg/l as N	7290	7200	84
SCN^-, mg/l	445	-	-
Daphnia Toxicity			
24-hr LC50, %	0.076	0.44	2.6
48-hr LC50, %	0.050	0.24	1.55
96-hr LC50, %	0.038	0.23	1.38
CHO Cytotoxicity			
LC50, %	0.055	0.4	

*Batch 2, full-strength

**n-Butyl acetate; 1/10 solvent/water ratio, 3X; air-stripped to eliminate butyl acetate

***pH adjustment with NaOH, air-stripped to expel NH_3, pH re-adjustment with HCl

CONCLUSIONS

A comparison has been made between a real coal gasification wastewater from a fixed-bed atmospheric gasifier and a simulated coal conversion wastewater. The simulated wastewater was similar with respect to the concentrations of TOC, COD, and phenols, but the real wastewater had an appreciably higher ammonia content. In addition, the real wastewater was approximately 4 to 5 times more toxic than the simulated wastewater, based on Daphnia, fish, and CHO bioassays.

The real wastewater was biologically-treatable when diluted to quarter-strength. Treatment in an activated sludge reactor with a 20-day sludge age and a 10-day hydraulic residence time resulted in residual concentrations of phenols generally below 1 mg/l, TOC removals of approximately 65%, and COD removals of approximately 63%. The effluent TOC and COD concentrations, however, were approximately 2 to 3 times higher than those in the effluent from an activated sludge reactor treating the simulated coal conversion wastewater under parallel operating conditions. Additionally, while the toxicity of the real coal conversion wastewater to Daphnia, fish, and mammalian cells was reduced appreciably by biological treatment and the mutagenicity of the wastewater was reduced to undetectable levels, the effluent was significantly more toxic than the biologically-treated, simulated wastewater effluent.

A significant portion of the residual TOC (approximately 30%) in the filtered activated sludge effluent following treatment of the real wastewater consists of organic compounds with a molecular weight greater than 30,000. If the effluent is to be re-used and concentrated in a cooling tower, the presence of this relatively large amount of high molecular weight material may have an adverse impact on the operation of the cooling towers.

Post-biological treatment involving ammonia-stripping and activated carbon adsorption significantly alleviated the mammalian cytotoxicity of the real wastewater; such treatment had no effect on the toxicity of the wastewater to Daphnia. Ozonation improved the gross chemical quality of the wastewater, but had an adverse impact on Daphnia toxicity.

ACKNOWLEDGEMENTS

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TREATMENT OF FOSSIL FUEL DERIVED WASTEWATERS WITH POWDERED ACTIVATED CARBON/ACTIVATED SLUDGE TECHNOLOGY

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ABSTRACT

The treatment of high strength fuel conversion wastewaters by conventional biological treatment processes may be operationally troublesome and only marginally effective from the standpoint of treatment system stability and performance. The addition of powdered activated carbon to the activated sludge process not only greatly improves product water quality but also provides cost savings compared to more conventional waste treatment and carbon regeneration processes.

This paper describes the powdered carbon/activated sludge wastewater treatment process, discusses the advantages of powdered carbon addition including performance obtained on fossil fuel derived wastewaters, and presents cost comparison data for wastewater treatment and spent carbon regeneration.

INTRODUCTION

Development of the synthetic fuels production industry is contingent in part on successful treatment of the production wastewaters since environmental regulations for treated wastewater discharges are likely to be very stringent and effluent reuse will be necessary in many facilities. Efficient, reliable waste treatment is of critical concern due to the constituents present in most synfuels wastes and the variability anticipated. These concerns have spurred investigation of powdered activated carbon addition to the activated sludge wastewater treatment process for improved treatment performance* and improved organics removals** among others.

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* Luthy, R.G., Stamoudis, V.C., and Campbell, J.R., "Removal of Organic Contaminants from Coal Conversion Condensates." Presented at the 54th Annual WPCF Conference, Detroit, Michigan (October, 1981).

** Wei, I.W., and Chen, J.C.Y., "Fate of Organics in the Treatment of Oil Shale Retort Water." Presented at the 54th Annual WPCF Conference, Detroit, Michigan (October, 1981).

The addition of powdered carbon to the activated sludge process, termed PACT*, provides enhanced treatment performance and reliability over that found in pure biological treatment systems. The addition of PAC provides improved COD removals and permits nitrification of the synfuels wastewater.

When Wet Air Carbon Regeneration is applied to the PACT process, the process is called the Wastewater Reclamation System (WRS) and is hereafter referred to as such.

Application of Wet Oxidation to synthetic fuels wastes, for spent carbon regeneration of solids wasted from the Wastewater Reclamation System and for oxidation of concentrated production wastes, enables economical disposal of concentrated, difficult to treat wastes and provides cost-effective spent carbon regeneration.

TREATMENT CONCEPTS

The addition of powdered activated carbon (PAC) to the activated sludge process combines simultaneously the advantages of physical adsorption and biological stabilization in the same "biophysical" treatment system. The presence of the active adsorbent (PAC) provides removal of non-biodegradable, adsorbable organics in the waste stream--organics which would otherwise escape untreated from a pure biological system. Furthermore, the high concentration of activated carbon in the treatment system ensures maintaining reasonable treatment even if biological upset should occur.

The benefits of adsorption and biodegradation are exploited by combining both methods of treatment in a single operation. The combined effects are illustrated in Figure 1 which shows carbon adsorption isotherms of two wastes, A and B. Waste A (solid line) is treatable by carbon adsorption as indicated by the shallow slope of the isotherm. Waste B is not readily treatable by activated carbon as indicated by the steep slope of the isotherm. Waste B apparently contains organic constituents which are not readily adsorbable.

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* PACT is a registered servicemark of DuPont.

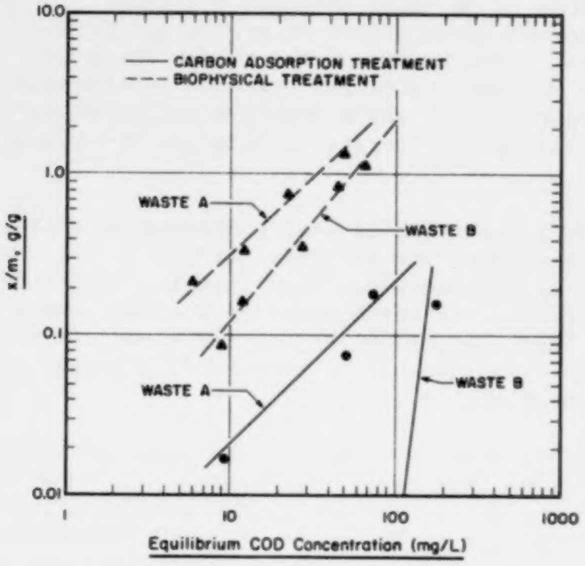


Figure I. PHYSICAL AND BIOPHYSICAL ISOTHERMS

The dashed lines show isotherms for the same two wastes when both biological treatment and adsorption are simultaneously imposed. Waste B is now treatable as indicated by the similarity of the two isotherms. In addition, considerably higher organic loading rates are obtained resulting in a smaller wastewater treatment system. The activated sludge has aided the activated carbon in removing organic constituents which are not readily adsorbable. For synfuels wastes, most of the particularly obnoxious fossil fuel related components such as multi-phenolics are adsorbable and are effectively removed in biophysical treatment. Performance of the Wastewater Reclamation System on synfuels wastewaters indicate that greater than 95 percent removal of COD can be obtained with only very low COD residuals remaining following treatment.

In addition to enhanced performance and increased organic loading rates, PAC addition to activated sludge adsorbs toxic or inhibitory components enabling the micro-organisms to function efficiently. This is important since synfuels wastewaters frequently contain toxic components in sufficient concentration to inhibit metabolic rates and nitrification. Further, carbon acts as a toxic sink to dampen organic fluctuations resulting from production process variations or upset.

The presence of PAC also provides a catalytic or perhaps best termed an alleo-catalytic effect on biological treatment. The active adsorbent concentrates on the PAC surfaces the extra-cellular enzymes needed for organics assimilation in addition to adsorption of waste organics and molecular oxygen. This concentration effect serves to catalyze the biological mechanisms.

Perhaps more important is that contaminants that are slow to degrade will be held by the activated carbon in the treatment system for the solids residence time, not the much shorter hydraulic residence time which would be the case where carbon is not present. Thus, additional organics are removed biologically which would otherwise have to be treated by granular carbon, ion exchange or ozonation.

The foregoing arguments explain the superior performance seen in powdered carbon/activated sludge systems on a micro-basis. However, there are some important design considerations that contribute to the success of the process. Of primary importance is the settleability of the sludge. The carbon nucleus of the floc particles serves as a weighting agent. The sludge can be readily settled and compacted and therefore carried at very high levels in the aeration basins. The Wastewater Reclamation System will typically operate at 15-25,000 mg/l mixed liquor suspended solids whereas a conventional activated sludge system is typically 2,000-4,000 mg/l. Though a major fraction of the WRS mixed liquor is PAC, volatile biological solids levels easily exceed conventional activated sludge systems and may approach 7,000 mg/l in normal operation.

THE WASTEWATER RECLAMATION SYSTEM

The Wastewater Reclamation System has been or will be used in numerous applications and will treat a wide variety of wastewaters including night soil, combined domestic and textile wastes, nitrification of domestic and industrial wastes, pharmaceutical wastes and organic chemicals wastes. A list of WRS applications and the waste treated are shown in Table 1.

TABLE 1. WRS INSTALLATIONS

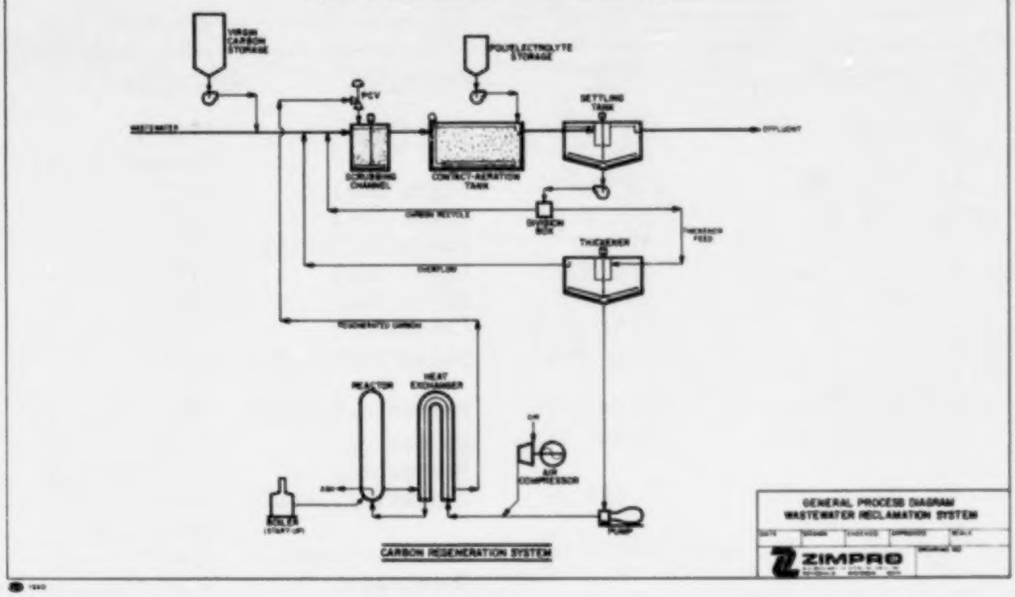
Location	Size	Wastewater	Operation
Rothschild, WI	3785 m^3/d	Domestic	1972-73 Demonstration
Kimitsu, Japan	500 KL/d	Night Soil	1975
Oga, Japan	1200 Kl/d	Night Soil	1977
Vernon, CT	24600 m^3/d	Domestic/Textile	1979
Senroku, Japan	1400 KL/d	Night Soil	1980
Oizumi, Japan	800 KL/d	Night Soil	1980
Medina, OH	37850 m^3/d	Domestic	1981
Burlington, NC (East Plant)	47300 m^3/d	Domestic/Textile	1981
Mt. Holly, NJ	18425 m^3/d	Domestic/Textile	1981
Kalamazoo, MI	204400 m^3/d	Domestic/ Pharmaceutical	Under Construction
Burlington, NC (South Plant)	35960m^3/d	Domestic/Textile	Under Construction
East St. Louis, IL	102200 m^3/d	Domestic/Organic Chemicals	Under Construction
Ibaragi, Japan	1520 KL/d	Night Soil	Under Design
El Paso, TX	37850 m^3/d	Domestic	Under Design
Bedford Heights, OH	11350 m^3/d	Domestic/ Industrial	Under Design
North Olmsted, OH	26500 m^3/d	Domestic/ Industrial	Under Design

The WRS flow scheme is presented in Figure 2. Typical major process components include aeration, clarification and optional effluent filtration. Auxiliary process components include dry carbon storage and liquid polymer addition.

When using WRS, the wastewater is aerated in the presence of a high concentration of powdered activated carbon (PAC), from 4,000 to 12,000 mg/L, depending on the influent wastewater characteristics and effluent quality required. The powdered carbon not only acts as an adsorbent, but also as a weighting agent, enhancing MLSS settling and enabling higher concentrations of volatile biological solids to be maintained under aeration. Thickened clarifier underflow solids, at concentrations typically ranging from 3.0 to 5.0 percent are recycled to the inlet of the aeration basin. Due to the high concentrations of PAC and biological solids maintained in the WRS, a high degree of reliable treatment is obtained.

The excess secondary sludge from the WRS is wasted from the aeration tank or clarifier to a gravity thickener. The thickened

Figure 2. WASTEWATER RECLAMATION SYSTEM


VIRGIN CARBON STORAGE
POLYELECTROLYTE STORAGE
PCV
SETTLING TANK
WASTEWATER
EFFLUENT
SCRUBBING CHANNEL
CONTACT-AERATION TANK
CARBON RECYCLE
DIVISION BOX
THICKENER FEED
THICKENER
OVERFLOW
REGENERATED CARBON
REACTOR
HEAT EXCHANGER
AIR
AIR COMPRESSOR
BOILER (START-UP)
PUMP
CARBON REGENERATION SYSTEM
GENERAL PROCESS DIAGRAM WASTEWATER RECLAMATION SYSTEM
ZIMPRO

underflow solids, at a concentration of 6.0 percent suspended solids or greater, is pumped to the regeneration unit heat exchangers by the high pressure pump at a pressure of approximately 50 kg/cm^2 (800 psig).

Compressed air is added to the carbon slurry flow prior to the heat exchangers. The combined slurry and air mixture passes through the heat exchangers where its temperature is raised prior to entering the reactor. In the reactor, the volatile biological solids and sorbed organics contained in the carbon slurry are 'wet oxidized.'

Since a net heat gain (temperature rise) occurs during the wet oxidation reactions, autothermal (thermally self-sustaining) operation is obtained. The hot regenerated slurry is then passed through the heat exchangers to recover the produced heat. The cooled regenerated slurry flows to the pressure reducing station and returned to the wastewater flow via a distribution diffusor in the scrubbing channel. Though a nearly complete oxidation (85-95%) of chemical oxygen demand occurs during regeneration, a small amount of low molecular weight residual organics remain which are returned directly to the treatment system for biological stabilization. Since these organics are readily biodegradable and comprised of weak acids, separate sidestream treatment of the regeneration recycle stream is not required.

Control of the mixed liquor suspended ash concentration is provided by regeneration reactor blowdown. Inerts accumulate at the reactor bottom and are vented from the reactor during steady-state operation and disposed. Since these materials are inert and 'wet oxidized' during regeneration, disposal as a non-hazardous material is generally acceptable.

A steam generator is included in the regeneration system to provide start-up steam requirements.

Wet air regeneration losses of volatile PAC are less than 5 percent of throughput, substantially less than PAC oxidation losses in conventional thermal regeneration processes. Regeneration losses include both those resulting from oxidation losses and reactor inerts blowdown to disposal. Powdered carbon losses of 1 to 5 percent and autothermal regeneration system operation have been confirmed in the full scale operations at Kimitsu, Japan* and Vernon, CT.**

ADVANTAGES TO SYNFUELS WASTE TREATMENT

Major advantages of the Wastewater Reclamation System to the treatment of fossil fuel derived wastewaters are the excellent product water quality obtained and the reliable treatment process operation and stability that is ensured with PAC addition. Treatment process stability is of major significance to the synfuels facility since biological treatment difficulties resulting in upset conditions will likely curtail fuel production, will result in post-biological treatment difficulties in reuse applications, and will result in failure to meet discharge requirements where direct effluent discharge is practiced.

Since the treatment system effluent quality is a major consideration in most synfuels applications, for both effluent reuse in the facility and for direct discharge, optimum performance is extremely important. Residuals (COD, ammonia) are of concern in terms of fouling reverse osmosis membranes, evaporator tubes and cracking and carbonizing in boilers and superheaters. Ammonia generally presents corrosion problems in cooling water systems and boilers. Organic priority pollutants present in coal derived wastewaters (see Table 2) represent a potential health hazard in the plant and must be effectively removed before direct discharge.

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* Meidl, J.A.; Berndt, C.L. and Nomoto, K., "Experience with Full Scale Wet Oxidation of Spent Carbon from the 'PACT' Process." Presented at the 51st Annual Conference of the WPCF, Anaheim, CA, (October, 1978).

** Pitkat, C.A. and Berndt, C.L., "Textile Waste Treatment at a Municipal PACT Facility." Presented at the 35th Purdue Conference, Purdue University, West Lafayette, IN, (May, 1980).

Enhanced organics (BOD_5, COD) removals and biological nitrification are obtained when powdered carbon is added to activated sludge. In numerous treatability demonstrations, improved organic removals of chemical wastes were obtained*, efficient nitrification was obtained in the WRS whereas biological treatment was unsuccessful due to the presence of pharmaceuticals** and nitrification of toxic wastes was possible in a two stage WRS mode***.

TABLE 2. LEVEL OF ORGANIC PRIORITY POLLUTANTS DETECTED IN EPA SCREENING PROGRAM

Priority Pollutant No.	Name	No. of Samples	Mean (mg/L)	Minimum Value (mg/L)	Maximum Value (mg/L)
1	* Acenapthene	18	216.8	0.013	3,000.0
39	* Fluoranthene	21	147.7	0.011	1,400.0
81	* Phenanthrene	36	130.2	0.010	3,200.0
80	* Fluorene	25	80.2	0.011	1,400.0
3	Acrylonitrile	9	65.7	0.043	330.0
84	* Pyrene	26	61.4	0.010	1,100.0
55	* Naphthalene	59	43.4	0.010	1,200.0
64	Pentachlorophenol	35	37.5	0.012	680.0
11	1,1,1-trichloroethane	93	26.0	0.010	1,300.0
74	* 3,4-benzofluoranthene	4	24.8	0.010	99.0
76	* Chrysene	27	24.3	0.010	440.0
49	Trichlorofluoromethane	27	22.4	0.011	290.0
75	* Benzo(k)fluoranthene	9	22.1	0.011	99.0
59	2,4-dinitrophenol	16	17.8	0.011	230.0
72	* Benzo(a)anthracene	23	15.8	0.010	180.0
78	* Anthracene	35	15.1	0.010	510.0
79	* Benzo(ghi)perylene	8	14.0	0.013	84.0

* Coal Based.

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* Sago, W.L. and Foresman, M.R., "Joint Municipal/Industrial Wastewater Treatment - Metro East St. Louis, Illinois." Presented at the 53rd Annual Conference of the WPCF, Las Vegas, Nevada (September, 1980).

** Sampayo, F.F. and Hollopeter, D.C., "The Influence of Industrial Waste on Nitrification." Presented at the 33rd Purdue Conference, Purdue University, West Lafayette, IN (May, 1978).

*** Frohlich, G., Ely, R.B. and Vollstedt, T.J., "Performance of a Biophysical Treatment Process on a High Strength Industrial Waste." Presented at the 31st Purdue Conference, Purdue University, West Lafayette, IN (May, 1976).

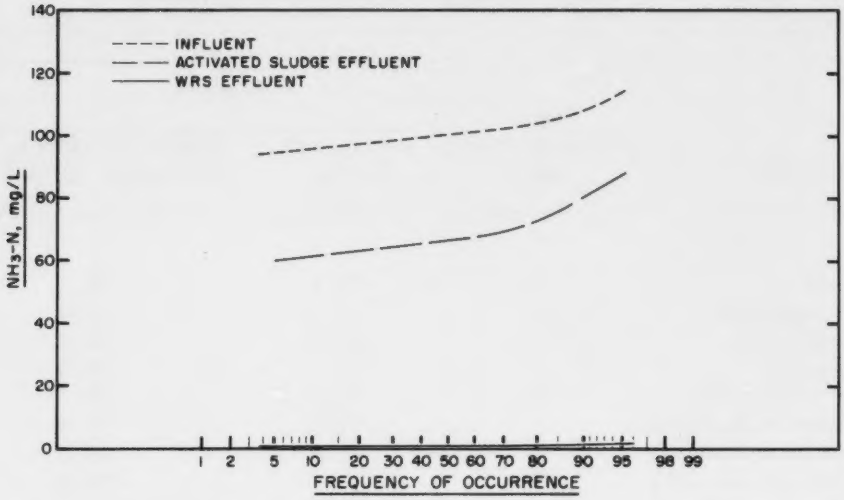

Figure 3. FREQUENCY PLOT OF AMMONIA REMOVAL

Recent performance on fossil fuel derived wastewaters wherein nitrification was required show that complete nitrification is readily obtained with PAC addition but is not obtained in a pure biological activated sludge system even at a long solids residence time and hydraulic detention time. A comparison of nitrification performance of activated sludge and WRS is shown in Figure 3. Both processes were operated in a single stage mode at an SRT of 35 days, however, the activated sludge pilot plant hydraulic detention time exceeded 50 hours more than two times the WRS.

A performance comparison of priority pollutant removals from conventional activated sludge and the powdered activated carbon/activated sludge process is shown in Table 3.* Improved priority pollutant removals were obtained with PAC addition.

Similar results, an approximate one-third greater priority pollutant removal with PAC enhanced sludge, has been demonstrated for shale oil retort wastewaters.**

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* Hutton, D.G., "Removal of Priority Pollutants with a Combined Powdered Activated Carbon - Activated Sludge Process." Presented at the 179th National AIChE Meeting, Houston, TX (March, 1980).

** Wei, op. cit.

TABLE 3. EFFLUENT PRIORITY POLLUTANT COMPARISON

Compound	Feed Concentration ppb	% Removal	
		Activated Sludge	Powdered Carbon/ Activated Sludge
Benzene	81	98.5	99.6
Chlorobenzene	3,660	99.1	99.8
Chloroethane	667	99.8	99.9
Chloroform	72	96.7	96.9
Methyl Chloride	138	98.5	99.7
Tetrachloroethylene	33	99.5	99.5
1,2-Dichlorobenzene	18	90.6	99.0
2,4-Dinitrotoluene	1,000	31.0	90.0
2,6-Dinitrotoluene	1,100	14.0	95.0
Nitrobenzene	330	94.5	99.9
1,2,4-Trichlorobenzene	210	99.9	99.9
2,4-Dichlorophenol	19	0	93.0
2,4-Dinitrophenol	140	39.0	99.0
4-Nitrophenol	1,100	25.0	97.0

Resiliency to potential toxic upsets due to production process malfunctions is illustrated in Figure 4. Consistent WRS performance is maintained in the two stage system though the total phenol concentration reached 2000 mg/L in the coal gasification liquor feed for a 1.0 hour duration. This was preceeded by a 0.5 hour period at 1000 mg/L total phenol, to simulate actual shock phenol levels occurring in a process malfunction. The results of Figure 4 show that the WRS effluent NH_3-N and total phenol levels remained low though no WRS operational adjustments were made to compensate for the shock loading. Consistent results continued beyond that shown in Figure 4. The effluent NH_3-N levels returned to less than 0.5 mg/l following the stress tests. Improved response would be expected with SRT changes during stress conditions.

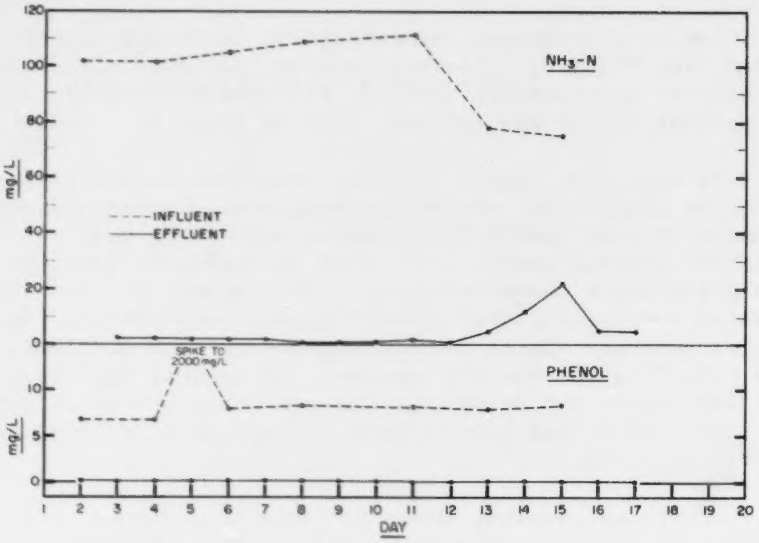

Figure 4. RESPONSE TO PHENOL SHOCK LOADING

PERFORMANCE

Initial WRS treatability investigations were conducted on coke oven gas flushing liquors -- quite similar to synfuels wastewaters. A performance comparison from studies of activated sludge and WRS treating these high strength liquors is shown in Table 4. The results indicate good performance for both processes, however, ammonia conversion to nitrate nitrogen was not obtained in the activated sludge treatment. Nitrification was obtained in the single stage WRS despite the high phenol concentration (468 mg/L total phenol) and the high waste COD level.

TABLE 4. PERFORMANCE COMPARISON:
COKE OVEN GAS FLUSHING LIQUORS

	Activated Sludge		WRS	
	Influent	Effluent	Influent	Effluent
BOD_5, mg/l	650	10	1050	4
COD, mg/l	1329	436	2359	289
NH_3-N, mg/l	600	731*	13	<1
SCN, mg/l	130	3.5	279	<2
Phenol, mg/l	150+	<1	468	<1
Cyanide, mg/l	--	--	7	1.2

*SCN is biologically converted to NH_3-N, there is no nitrification.

Subsequent treatment demonstrations confirmed nitrification of coke oven flushing liquors at solids residence times as low as 7 days at approximately 25°C.* Wastewater characteristics were similar to the WRS influent data of Table 4.

More recently, Zimpro Inc. has conducted treatability studies on fossil fuel derived wastewaters. Laboratory scale treatment of coal gasification wastes were performed. Additional process wastes were added to duplicate expected full scale plant waste characteristics. Both single and two stage activated carbon/activated sludge systems were operated for organics removal. Spent carbon regeneration was provided. Since nitrification was not required, pH control and alkalinity supplement were not provided. The raw waste pH was slightly less than 5 while the mixed liquor and effluent pH levels were approximately 6.5.

Performance results, shown in Table 5, indicate good organic removals for both single and two stage systems.

TABLE 5. WRS PERFORMANCE: COAL GASIFICATION WASTEWATER

	Single Stage		Two Stage	
	Influent	Effluent	Influent	Effluent
BOD$_5$, mg/l	699	<12	708	<12
COD, mg/l	1580	110	1560	94
TKN, mg/l	148	110	152	116
NH$_3$-N, mg/l	104	88	103	93
Phenol, mg/l	6.9	<0.9	6.7	<1.0
Cyanide, mg/l	10.0	0.17	10.8	0.14

Similar laboratory scale treatment of a coal gasification wastewater in a nitrification mode with intermittent NaOH supplement for pH control provided the results shown in Table 6. The pH adjustment maintained a minimum pH of 6.5. The wastewater in this study contained a higher volatile acids fraction than the previous gasifier waste resulting in a higher BOD/COD ratio. In addition to nearly complete nitrification in both single and two stage treatment modes, substantial denitrification is demonstrated.

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* Bauer, G.L., Hardie, M.G. and Vollstedt, T.J., "Biophysical Treatment of Coke Plant Wastewaters." Presented at the 35th Purdue Conference, Purdue University, West Lafayette, IN (May 1980).

TABLE 6. WRS PERFORMANCE: COAL GASIFICATION WASTEWATER

	Single Stage		Two Stage	
	Influent	Effluent	Influent	Effluent
BOD_5, mg/l	1344	<6	1344	<4
COD, mg/l	2270	45	2270	53
TKN, mg/l	99	5.5	99	5.7
NH_3-N, mg/l	70	<1.1	70	<1.0
Phenol, mg/l	2.6	<0.1	2.6	<0.1
Cyanide, mg/l	7.5	0.08	7.5	0.11

An extensive design study on a larger scale pilot basis was conducted on the gasifier wastewater of Table 6. Performance results over the 6 month study period were excellent with a neglible effluent NH_3-N concentration from the two stage WRS.

TREATMENT COST COMPARISON

Cost comparisons (Table 7) of WRS and more conventional biological treatment processes, sponsored by the EPA, show the WRS is approximately cost equivalent to conventional activated sludge and activated sludge designed for nitrification.* Considerable cost savings is obtained employing WRS in-lieu of activated sludge followed by granular carbon adsorption.

TABLE 7. TREATMENT COST COMPARISON

	Cost, $/1000 Gallons		
Process	5 mgd	10 mgd	25 mgd
WRS*	0.52	0.40	0.30
Activated Sludge			
Conventional	0.49	0.38	0.29
Single Stage Nitrification	0.51	0.41	0.31
Two Stage Nitrification	0.59	0.46	0.35
Granular Carbon System @ 1500 lb carbon/MG	0.73	0.58	0.46

* Designed to nitrify.

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* Culp, G.L. and Shuckrow, A.J., "Appraisal of PAC Processes for Municipal Wastewater Treatment." Environmental Protection Technology Series, EPA-600/2-77-156, Contract No. 68-03-2211 (September, 1977).

Investigation of secondary treatment options for Lurgi process coal gasification liquors including the powdered activated carbon/activated sludge process and other applicable wastewater treatment processes showed the PAC/activated sludge process employing Wet Air Regeneration the most cost effective treatment option (see Table 8).* The annual operating cost of the PAC/activated sludge process is comparable to conventional biological treatment with land application of waste sludges, while considerable capital cost savings are obtained. The net energy requirements of the PAC treatment system is also equivalent to conventional activated sludge.

TABLE 8. TREATMENT COST COMPARISON FOR LURGI PROCESS WASTES*

Treatment Process	Capital Cost	Annual Operating Cost	Net Energy Requirements, KWH/yr
PAC/Activated Sludge			
Wet Air Regeneration	5,788,000	1,764,000	18,066,920
Multiple Hearth Regeneration	6,761,000	2,460,000	23,030,900
Activated Sludge			
Incineration of Sludges	9,862,000	2,347,000	26,115,400
Land Application of Sludges	6,769,000	1,799,000	18,401,500

* Based on 242 MM SCF PD SNG

The results of Table 8 show considerable spent carbon regeneration cost savings with Wet Air Regeneration over that obtained with multiple hearth regeneration.

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* Castaldl, F.J., "Application of Combined Powdered Carbon/Activated Sludge Treatment to Lurgi Process Coal Gasification Wastewaters." Application of Adsorption to Wastewater Treatment, Vanderbilt University, Nashville, TN (February, 1981).

CONCLUSIONS

The addition of powdered activated carbon to the activated sludge process, including spent carbon reactivation by Wet Air Regeneration, provides improved treatment performance and ensures stable reliable operation. The addition of PAC provides further treatment benefits including resistance to shock loading and wastewater toxicity and permits nitrification of synfuels wastewaters.

Performance of the Wastewater Reclamation System on coke oven gas flushing liquors and coal gasification process liquors is excellent. Both organic treatment and nitrification of these wastewaters were demonstrated.

Cost evaluations of the Wastewater Reclamation System on coal gasification wastewaters show the WRS cost effective compared to conventional biological treatment with land application of residuals. Wet Air Regeneration was shown more economical than multiple hearth regeneration for spent powdered carbon regeneration.

LAND TREATMENT OF COAL CONVERSION WASTEWATERS

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ABSTRACT

This research project investigated the treatment potential of soil systems for polynuclear aromatic compounds (PNAs) present in aqueous wastes from coal conversion processes. A protocol for obtaining the soil assimilative capacities for mutagenic and recalcitrant PNA compounds was developed and, for a subset of compounds, data were obtained to describe: (1) rates of transformation, including degradation, detoxication, and possible intoxication; (2) effect of PNA structure on transformation rate; (3) effect of engineering management options, including nutrient addition, analog enrichment, surfactant addition, and pH adjustment on transformation rates; and (4) soil acclimation to PNAs.

A three-step protocol including: (1) incubation, (2) identification, and (3) determination of mutagenic potential involves interfacing high performance liquid chromatography (HPLC) for compound and metabolite identification with the Ames Salmonella typhimurium/mammalian microsome mutagenicity assay for determining genotoxic potential of PNA compounds and transformation products in soil. Identification (HPLC) and mutation (Ames assay) were quantified.

INTRODUCTION

This research has investigated the use of land treatment for the polynuclear aromatic (PNA) class of compounds present in wastes from the coal gasification industry. Land treatment has been demonstrated to be a cost-effective environmentally safe technology for a multitude of industrial wastes. PNA compounds have been identified as byproducts in the synfuel industry, and are of critical environmental concern due to the following specific characteristics: (1) chronic health effects (carcinogenicity), (2) microbial recalcitrance, (3) high bioaccumulation potential, and (4) low removal efficiencies in traditional wastewater treatment processes (Herbes et al., 1976). Therefore, a preliminary feasibility assessment regarding the application of land treatment technology for coal conversion wastes in general and for hazardous components in particular was undertaken.

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In a comprehensive review of the literature Sims and Overcash (1981) summarized the behavior and fate of PNA compounds in terrestrial systems, including soils and vegetation. The potential for effective treatment and safe ultimate disposal of PNA compounds is significant with regard to land application of coal gasification wastes.

Land application is defined for the purpose of this study as the intimate mixing or dispersion of wastes and the soil-plant system with the objective of microbial stabilization, adsorption, immobilization, selective dispersion, or crop recovery leading to an environmentally acceptable assimilation of the waste. In this case coal conversion wastes are applied in thin layers over land areas to provide intensive waste constituent interaction with the soil, with substantial soil zones between waste and relevant surface and ground waters, for the purpose of environmentally acceptable assimilation.

Land application of synfuel wastes is also based on a constraint of nondegradation of land. That is, the waste when considered on a constituent-by-constituent basis shall be applied to the plant-soil system at such rates or over such time spans that no land is irreversible removed from some other potential usage (agriculture, development, forestation, etc) (Overcash and Pal, 1979).

There are four major stages in the design of a total waste management system for coal conversion wastes. These stages, shown in Figure 1 are:

I. the determination of the land limiting constituent (LLC) or that parameter or class of parameters requiring the largest land area for assimilation;

II. the design evaluation of all required components for the land application system and the cost analysis based on different amounts of the LLC;

III. the selection and cost analysis of pretreatment or in-plant alternatives for reducing the total level of the LLC;

IV. the economic balance between the cost of the total land receiver and the cost of pretreatment processes such that the sum total system costs is a minimum (Overcash and Pal, 1979).

The first stage of the design methodology is the most difficult. The assimilative capacities for PNAs have not been established. An objective of this research project has been to obtain the information necessary to complete stage one for the coal gasification industry. This has required a detailed literature review of coal gasification waste characterization and plant-soil assimilative capacities for waste constituents, and laboratory studies to determine the soil assimilative capacities for relevant PNAs.

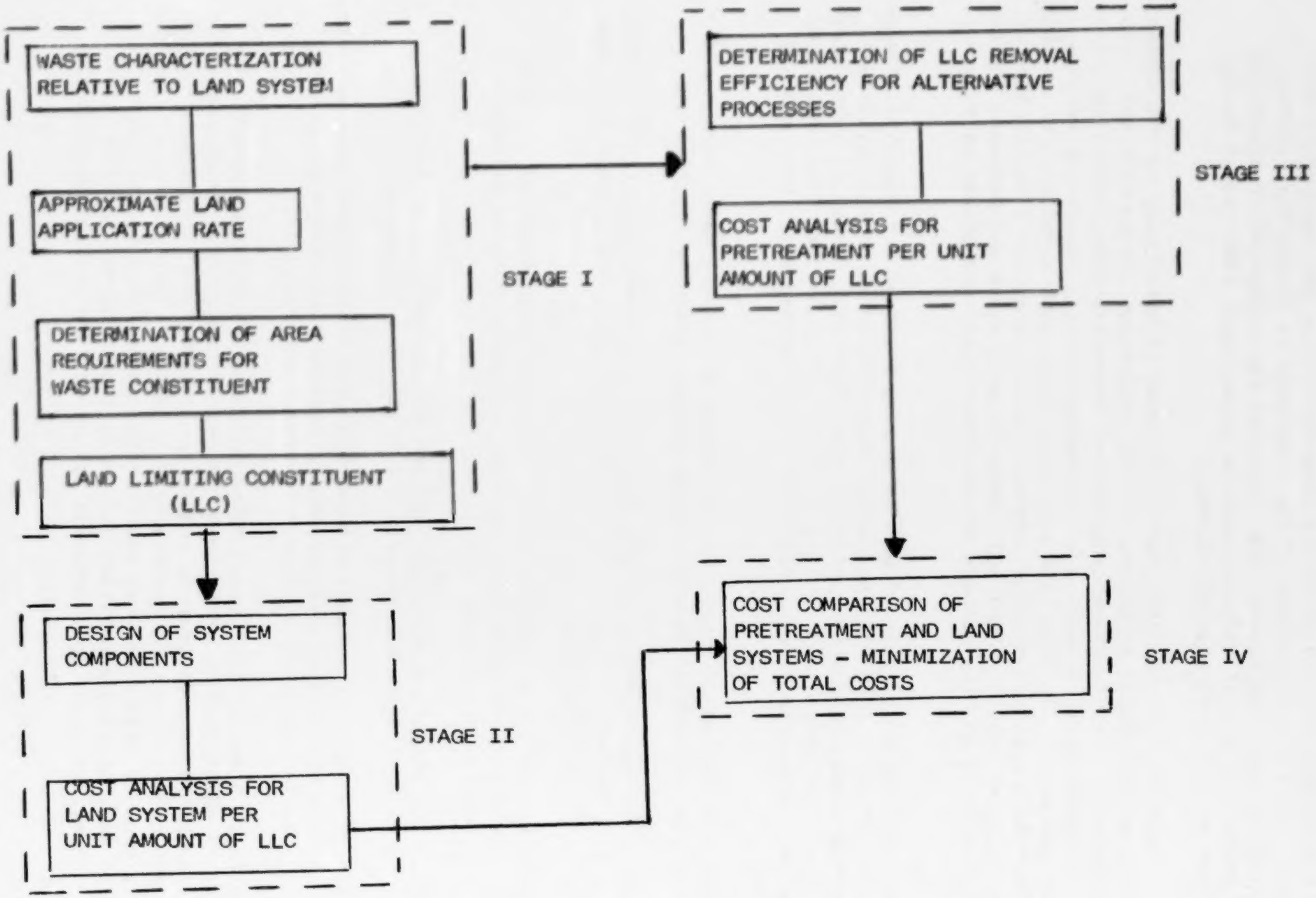
WASTE CHARACTERIZATION RELATIVE TO LAND SYSTEM
APPROXIMATE LAND APPLICATION RATE
DETERMINATION OF AREA REQUIREMENTS FOR WASTE CONSTITUENT
LAND LIMITING CONSTITUENT (LLC)
STAGE I
DETERMINATION OF LLC REMOVAL EFFICIENCY FOR ALTERNATIVE PROCESSES
COST ANALYSIS FOR PRETREATMENT PER UNIT AMOUNT OF LLC
STAGE III
DESIGN OF SYSTEM COMPONENTS
COST ANALYSIS FOR LAND SYSTEM PER UNIT AMOUNT OF LLC
STAGE II
COST COMPARISON OF PRETREATMENT AND LAND SYSTEMS - MINIMIZATION OF TOTAL COSTS
STAGE IV

Figure 1. Stages of Unified Methodology for Design of Pretreatment-Land Application Systems.

APPROACH

Stage one of the four-stage methodology required the following information: (1) waste characterization on a constituent-by-constituent basis; (2) determination of the plant-soil assimilative capacity for each waste constituent or component; (3) determination of the land area requirements for each waste component or class of components; and (4) determination of the land limiting constituent (LLC), which is that constituent or class of constituents requiring the largest land area for safe treatment and ultimate disposal.

The waste characterization for each constituent is expressed as kg/unit time, while the assimilative capacity is expressed as kg of parameter/unit area/unit time. The ratio of waste generation to assimilative capacity is the area (hectares or acres) required for the environmentally acceptable waste application to the terrestrial system. Ranking the required land areas indicates one or more constituents as requiring the greatest land size, and this constituent or class of constituents is defined as the LLC. Using the LLC area guarantees that other waste constituents are applied at environmentally acceptable rates.

WASTE CHARACTERIZATION AND GENERATION

A review of the literature was conducted to obtain information concerning wastewater characterization in the coal gasification industry. Due to the experimental and developing nature of "the state of the art" of coal gasification, it has been impossible to obtain comprehensive information concerning:(1)coal mass flow rates, (2) water mass flow rates, and (3) concentrations of inorganic and organic species including toxic organic compounds (PNAs) in one assessment document or one coal gasification facility.

Waste constituents were identified, quantified, and waste generation rates (kg/yr) were calculated with information obtained for an expected typical full scale Lurgi coal gasification facility. That is, wastewater was characterized for a full scale Lurgi facility: 250 x 10^6 SCFD of medium to high BTU synthetic natural gas (SNG), operating at a coal feed rate of 2245 x 10^3 lb/hr and a condensate flow rate of 1897 x 10^3 lb/hr, and using North Dakota Lignite coal. Because of the dearth of information concerning PNA concentrations and mass flows in the literature surveyed, several calculational procedures were necessary to derive expected concentrations of PNAs in the wastewater addressed. Expected concentrations of PNAs were based on other waste constituents present. The result is a preliminary waste characterization including constituent identification and waste generation rates for over 90 individual constituents.

ASSIMILATIVE CAPACITIES AND LAND AREA REQUIREMENTS

Much information already exists with regard to the terrestrial assimilation capacities for several soil types for a multitude of organic and inorganic constituents identified in coal gasification wastewaters (Overcash and Pal, 1979; and Sims and Overcash, 1980). Information is especially abundant with regard to inorganic species identified. A large body of information exists indicating that PNAs are not generally biomagnified in vegetation and crops (Sims and Overcash, 1981). However, information concerning the soil assimilation of PNA constituents in coal gasification wastewaters needed to be developed for several PNA compounds.

With the information obtained an initial land limiting constituent analysis was conducted which did not take into account the PNA class of compounds. The LLC analysis for coal gasification wastewater identified cadmium as the constituent requiring the greatest land area (750 ha) for land treatment.

To determine the soil assimilative capacities (SACs) for PNAs in coal gasification wastes, it is necessary to determine realistic concentrations of PNAs that would result from the land application of a typical coal gasification waste. The land area determined in the initial LLC analysis provided the basis for calculating the resultant PNA concentrations in soil for each PNA compound. Waste generation for each PNA was calculated by multiplying the PNA concentration by the volumetric flow rate to obtain mass/time (kg/yr). The calculated waste generation was divided by the land area determined in the LLC analysis (750 ha) to obtain the resultant soil PNA concentration (mg/kg).

The effect of the presence of PNA compounds in coal gasification wastewater on land area requirements can be evaluated by experimentally determining the soil assimilative capacities. An evaluation of the SACs could determine whether an individual PNA compound or the class of PNAs required more or less land area for treatment than cadmium. With this information a design for land application for the safe treatment and disposal of hazardous and toxic components as well as other constituents in coal gasification wastes is assured by using the LLC approach.

EXPERIMENTAL DESIGN

Experiments to determine the SACs of PNA compounds present in coal gasification wastewaters were designed to obtain the following specific information: (1) rates of PNA transformation; (2) effect of PNA structure on transformation rate; (3) effect of engineering management options on transformation rate; (4) soil acclimation to PNAs; and (5) toxicity and genotoxic potential of soil-treated PNAs.

SELECTION OF PNA COMPOUNDS FOR STUDY

A subset of the total number of PNAs identified in coal gasification wastewaters was selected based on the following criteria: (1) genotoxicity, (2) molecular recalcitrance, (3) priority pollutant status, and (4) lack of information concerning fate and behavior in the environment. Soil concentrations for the PNAs considered based on the LLC analysis conducted are shown in Table 1. Waste PNA concentration, mass generation, and soil concentration resulting from land application using the LLC constraint (750 ha) are included. For those PNAs not quantified in the literature, the highest concentration on the list was used (0.57 mg/kg in soil).

TABLE 1. PNA COMPOUNDS AND SOIL CONCENTRATIONS

PNA Compound	Condensate Concentration (mg/l)	Waste Generation (kg/yr)	Soil Concentration (mg/kg)
Acenaphthylene	0.114	855	0.57
Dibenzofuran	-	-	0.57
Acridine	-	-	0.57
Anthracene	0.082	615	0.41
Benzo(b)fluoranthene	0.066	495	0.33
Benzo(k)fluoranthene	0.034	255	0.17
Benz(a)pyrene	0.072	540	0.36
Indeno(1,2,3-cd)pyrene	-	-	0.57

PNA COMPOUND APPLICATION

Each PNA compound was investigated as a separate solution applied on separate soil reactors. Compounds were applied to the soil in small volumes of solvent (methylene chloride), and were mixed thoroughly with the soil to simulate soil incorporation of applied wastes, and to obtain an even distribution of the PNA compound throughout the soil at the desired concentration. Triplicate reactors were used for each PNA.

SOIL TYPE

Norfolk fine sandy loam is a common soil type, typical of the coastal plain, used in land application systems in North Carolina. The Norfolk series is a member of the fine-loamy, siliceous, thermic family of Typic Paleudults.

ENVIRONMENTAL CONTROL CHAMBER

PNA compounds, at the indicated concentrations in 200g and 2000g soil in glass beakers, were incubated in an environmentally controlled chamber. Environmental parameters that were controlled included temperature (25 C), light exposure (dark to prevent photodegradation), and soil moisture (60-80% field capacity). Soil moisture was adjusted to 80% of field capacity with water. Water was added when the soil moisture capacity decreased to 60% of field capacity to simulate field conditions of wetting and drying.

ANALYTICAL METHODS

Soil Extraction and Sample Preparation

The extraction procedure used for extracting PNAs from soil was based on the high performance liquid chromatography procedure for analysis of PNA compounds in water samples (Federal Register, 1979). Soil moisture was adjusted to 80% field capacity prior to extraction. Methylene chloride (250 ml) was added to 200g soil. The solvent-soil mixture was homogenized for two minutes with a Tekmar Tissumizer. The supernatant was decanted from the soil reactor and filtered through anhydrous sodium sulfate. The filtrate was concentrated to a final volume of 3-5 ml.

Reverse Phase-UV HPLC Analysis

A Waters HPLC was utilized with acetonitrile-water as the mobile phase, and a C-18 Perkin Elmer Reverse Phase column was used as the stationary phase. PNA compounds were identified with a UV detector at a wavelength of 254 nm.

Sample Fractionation for Ames Assay

Soil extracts were fractionated using a C-8 preparative Lobar size A prepacked column. Polarity classes of degradation products were collected in acetonitrile-water, evaporated, and redissolved in dimethyl sulfoxide for the Ames assay.

BIODEGRADATION DETERMINATION

Kinetic parameters of interest with respect to biodegradation include half-life ($t_{1/2}$ in days), rate of transformation (r in kg PNA/ha-day), and the rate constant (k in day^{-1}). These kinetic parameters are directly related to the soil assimilative capacities for PNAs.

GENOTOXICITY

Polarity classes of soil PNA degradation products were tested with the Ames assay (Ames et al., 1975). This assay is widely used for the detection of potential carcinogenicity and mutagenicity of environmental chemicals. Toxicity and mutagenicity were determined and dose-response curves were developed. The assay was conducted with and without microsomal activation. Strain TA-98, which detects frameshift mutations, and strain TA-100, which detects base pair substitution mutations, were used.

ENGINEERING MANAGEMENT OPTIONS

Engineering management options, including analog enrichment, nutrient addition, surfactant addition, and pH adjustment are tools which the environmental engineer may use to stimulate biological activity and to increase the rate of biodegradation of recalcitrant compounds. With application of industrial wastes with low levels of substrate organics and PNAs, the level of microbial activity would be expected to be similar to that of the native soil. Engineering management options for organic constituents are potential accelerators of microbial activity. Since the soil assimilative capacity is directly related to the kinetics of degradation, increasing microbial activity may lead directly to increasing the soil assimilative capacities for PNA compounds in coal gasification wastes.

The effect of each engineering management option was tested separately. Addition of an analog-substrate (carbon and energy source) has been shown to increase general microbial activity and growth. Addition of the nutrients nitrogen and phosphorus, which influence the growth of microorganisms, to microbial cultures stabilizing compounds deficient in these elements has been demonstrated to increase the rate of stabilization. Since surfactants can be utilized to increase cell membrane permeability, surfactants may be useful in increasing the solubility and cell membrane permeability of PNAs with a resultant greater oxidation and degradation in the soil environment. These three amendments were investigated for their direct effect on PNA degradation kinetics.

Although increasing soil pH from less than seven to neutral generally increases microbial activity, it may be especially important in soil systems to encourage bacterial growth and competition vis-a-vis fungi. Major differences with respect to microbial oxidation pathways of aromatic hydrocarbons between bacteria and fungi are believed to exist with fungi, premoninant at low soil pH, possibly metabolizing PNAs to more genotoxic products than with bacteria (Dagley, 1975; Cerniglia et al., 1979). Since pH has a significant effect on soil bacterial/fungal proportions, pH may be an important engineering tool to direct the pathway of PNA degradation through a series of detoxication reactions. Soil pH was adjusted with calcium carbonate solutions to 7.0 in triplicate soil reactos.

Two PNA compounds chosen for intensive study with amendments were anthracene and benz(a)pyrene. Anthracene is a three ring aromatic hydrocarbon which serves as a carbon and energy source for microorganisms and is weakly carcinogenic. Benz(a)pyrene is a five ring aromatic hydrocarbon that has not been demonstrated to be a carbon and energy source, but is believed to be degraded through cometabolic processes. Benz(a)pyrene is a powerful carcinogen.

SOIL ACCLIMATION

Acclimation of the soil to each PNA compound was investigated by spiking the soil at zero, three, and six months. Rates of degradation were monitored for each time increment and were compared through time.

STATISTICAL ANALYSIS

Kinetic data were subjected to analysis of variance, and when significant differences at the five percent level were found among PNA compounds Duncan's New Multiple Range Test was employed to separate means. The statistical procedures were performed using standard package programs of Statistical Analysis Systems-76 (Barr et al., 1976).

RESULTS AND DISCUSSION

RATES OF PNA TRANSFORMATION

Table 2 presents results from the laboratory study for kinetic parameters for the biodegradation of PNAs during a 90-day incubation period. Results represent the average of triplicate reactors. Half-lives range from a low of 18 days for acenaphthylene and dibenzofuran to indeno(1,2,3-cd)pyrene which exhibited no measurable loss with time.

TABLE 2. LABORATORY DETERMINED KINETIC DATA FOR PNA DEGRADATION

PNA Compound	Number of Rings	Initial Concentration (mg/kg soil)	Half-life ($t_{1/2}$,days)	Rate Constant (k,day^{-1})	Rate ($\frac{mg}{kg-day}$)
Acenaphthylene	3	0.57	18^{A*}	0.039	0.022
Dibenzofuran	3	0.57	18^{A}	0.039	0.022
Acridine	3	0.57	102^{B}	0.007	0.004
Anthracene	3	0.41	34^{A}	0.017	0.007
Benzo(b)-fluoranthene	5	0.33	98^{B}	0.007	0.002
Benzo(k)-fluoranthene	5	0.17	89^{B}	0.008	0.001
Benz(a)pyrene	5	0.36	80^{B}	0.009	0.003
Indeno(1,2,3-cd)-pyrene	6	0.57	$-^{C**}$	**	**

*Values represent means of three replicates. Means followed by the same letter are not significantly different at the 0.05 level.

**No decrease in Indeno(1,2,3-cd)pyrene could be detected by HPLC.

Kinetic parametersfor other PNAs identified in coal gasification wastes which were not included in the laboratory study are given in Table 3. The information for these compounds was obtained in a comprehensive review of the literature (Sims and Overcash, 1981).

TABLE 3. LITERATURE VALUES FOR KINETIC DATA FOR PNA DEGRADATION

PNA Compound	Number of Rings	Initial Concentration (mg/kg soil)	Half-life ($t_{1/2}$,days)	Rate Constant (k,day^{-1})	Rate ($\frac{mg}{kg-day}$)
Naphthalene	2	7.0	0.12	5.78	40.4
Indole	2	500	1.0	0.693	364.5
Fluorene	3	0.9	39	0.018	0.016
Fluoranthene	4	16.5	143	0.005	0.080
Phenanthrene	3	2.1	26	0.027	0.056

Results for PNA degradation kinetics from the laboratory study and from the literature review indicate that most PNAs addressed have reasonable, finite half-lives in soil systems.

EFFECT OF PNA STRUCTURE ON TRANSFORMATION RATES

Table 2 summarizes the results of the statistical analysis of PNA compounds by structure and half-life. Arranging PNAs by number of rings and half-life indicates that there are three distinct, statistically significantly different groups of PNA compounds. The general trend is for lower ring compounds to exhibit faster degradation kinetics i.e., there is an inverse relationship between the number of rings (PNA size) and half-life.

These results are consistent with the findings of other researchers for aquatic and soil systems for other PNAs. Information developed here adds to the list of quantitative data available for environmental engineers concerned with the design of land treatment systems for the coal gasification industry.

EFFECT OF ENGINEERING MANAGEMENT OPTIONS ON TRANSFORMATION KINETICS

Results showing the effects of environmental management options on biodegradation kinetics for the PNAs studied in the laboratory are given in Tables 4 and 5.

TABLE 4. EFFECT OF AMENDMENTS ON ANTHRACENE DEGRADATION

Amendment	Half-life ($t_{1/2}$, days)	Rate Constant (k, day^{-1})	Rate ($\frac{mg}{kg\text{-}day}$)
None	42^{A*}	0.017	0.68
Nutrients	41^{A}	0.017	0.69
pH	41^{A}	0.017	0.69
Surfactant	45^{A}	0.015	0.63
Analog Enrichment	38^{A}	0.018	0.75

*Values represent means of three replicates. Means followed by the same letter are not significantly different at the 0.05 level.

The degradation of anthracene, a three ring PNA compound which serves as a substrate (carbon and energy source) for soil microorganisms, does not appear to be influenced by the engineering management options used in this study. Statistical analysis of the laboratory data indicate that the relatively short half-life for anthracene with no amendment addition is not statistically different from the half-lives for anthracene treatment with any of the amendments.

TABLE 5. EFFECT OF AMENDMENTS ON BENZ(a)PYRENE DEGRADATION

Amendment	Half-life ($t_{1/2}$, days)*	Rate Constant (k, day^{-1})	Rate ($\frac{mg}{kg\text{-}day}$)
None	90^{A}	0.0077	0.28
Nutrients	81^{A}	0.0082	0.31
pH	64^{B}	0.0108	0.39
Surfactant	87^{A}	0.0080	0.29
Analog Enrichment	64^{B}	0.0108	0.39

*Values represent means of three replicates. Means followed by the same letter are not significantly different at the 0.05 level.

The degradation of benz(a)pyrene, a five ring PNA compound, is considered to be cometabolized i.e., cannot serve as a source of carbon and energy for the growth of microorganisms, does appear to be influenced by the engineering management options used in this study. Statistical analysis of the data indicated statistically significant **differences** among the treatments. The amendments which effected a significant decrease in the half-life of B(a)P included analog enrichment and pH adjustment.

This information has direct implications for the design of land treatment systems for coal gasification wastes. The data suggest that it may be possible to influence the degradation rates of recalcitrant and hazardous organic compounds through engineering management options.

SOIL ACCLIMATION TO PNAs

Results for the acclimation of soil systems to PNA compounds are still being analyzed. Extent of acclimation appears to vary among the PNA compounds. Indeno(1,2,3-cd)pyrene showed the greatest acclimation from no measurable degradation to 360 days half-life to 201 days half-life for 3,6, and 9 months incubation respectively. More information must await additional data collection and statistical analysis.

TOXICITY AND GENOTOXIC POTENTIAL OF SOIL-INCUBATED PNAs

PNA parent compound, benz(a)pyrene and degradation products collected as polarity classes were not found to be toxic at concentrations from 10ug/plate to 500 ug/plate to be Salmonella typhimurium strains TA-98 and TA-100 used in this study,

Results for mutagenesis testing for B(a)P and degradation products are presented in Table 6. Data are given for the soil control, and at six months of incubation of B(a)P in soil.

TABLE 6. MUTAGENICITY OF SOIL-INCUBATED BENZ(a)PYRENE

Sample	Time (months)	Mutagenic Ratio at 500 ug/plate*			
		Without Activation		With Activation	
		TA-98	TA-100	TA-98	TA-100
Soil Control	6	1.81	1.20	1.84	1.72
Parent Compound (B(a)P)	6	1.37	1.09	7.82	3.16
Polar Class Fraction	6	1.18	1.26	2.96	1.50
Nonpolar Class Fraction**	6	1.28	1.15	3.72	2.19

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*Mutagenic Ratio is defined as a number of revertants with sample divided by the number of revertants without sample. A test compound or sample is considered negative if the mutagenic ratio is less than 2.0

**The Nonpolar class fraction was that fraction collected in preparative high performance liquid chromatography which appeared after the parent compound (B(a)P) for an elution gradient proceeding from more polar fractions to less polar fraction with increasing run time.

Results indicate that neither parent compound nor degradation products are mutagenic without mammalian microsomal activation. This is well known for B(a)P, but is not known for soil metabolites of B(a)P.

Results also indicate that the mutagenic potential of degradation products of soil incubated B(a)P are much less than the parent compound. The highest mutagenic potential (3.72) is associated with the Nonpolar class fraction.

This information suggests that after six months of soil incubation, the products of biodegradation of B(a)P are much less mutagenic than the parent compound. A detoxication pathway is therefore indicated for B(a)P biodegradation in soil.

CONCLUSIONS

Results from this preliminary study indicate that land application technology for fossil fuel wastes is promising. A protocol has been established for obtaining the soil assimilative capacities for recalcitrant and mutagenic PNA compounds, and for determining genotoxic potential of parent compounds and metabolites in soil. With the significant cost benefit for land treatment and the demonstrated potential to actually decompose recalcitrant and hazardous organics, it would apppear reasonable to proceed to further evaluations. Using this protocol a more detailed design based on specific waste characterization and site-specific analyses would follow for a particular sunfuel facility.

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Session III: AIR-RELATED ENVIRONMENTAL CONSIDERATIONS

Chairman: Theodore G. Brna
U.S. Environmental Protection Agency
Research Triangle Park, NC

PB83-128322

REMOVAL OF ACID GASES AND OTHER CONTAMINATES FROM COAL GAS † USING REFRIGERATED METHANOL

by

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and R. M. Felder

ABSTRACT

The steam-oxygen gasification of a New Mexico subbituminous coal was carried out in a pilot-scale fluidized bed gasifier. Gas cleaning was accomplished by a hot cyclone, a water quench-venturi scrubber, filters, and an acid gas removal system using refrigerated methanol as the solvent. Results of both gasification and gas cleaning are described. Refrigerated methanol proved to be effective in cleaning the gasifier make gas, however, the presence of several reduced sulfur species and hydrocarbons was detected in the absorber, flash tank, and stripper exit gas streams over a wide range of operating conditions. While a variety of simple aromatics accumulated in the recirculating methanol, essentially no polynuclear aromatic compounds were detected. Most polynuclear aromatic compounds were evidently removed in the gas quenching process.

INTRODUCTION

As a part of a continuing research program on the environmental aspects of fuel conversion, the U. S. Environmental Protection Agency has sponsored a research project on coal gasification at North Carolina State University in the Department of Chemical Engineering. The facility used for this research is a small coal gasification-gas cleaning pilot plant. The overall objective of the project is to characterize the gaseous and condensed phase emissions from the gasification-gas cleaning process, and to determine how emission rates of various pollutants depend on adjustable process parameters.

A complete description of the facility and operating procedures is given by Ferrell et al., Vol I, (1980), and in abbreviated form by Felder et al. (1980). A schematic diagram of the Gasifier, the Acid Gas Removal System (AGRS), and other major components is shown in Figure 1.

In an initial series of runs on the gasifier, a pretreated Western Kentucky No. 11 coal was gasified with steam and oxygen. The results of this work are given by Ferrell et al., Vol II, (1981), and were presented at the EPA Symposium on Environmental Aspects of Fuel Conversion Technology V, held in St. Louis, Mo., September, 1980.

The second major study carried out on the facility was the steam-oxygen gasification of a New Mexico subbituminous coal (from the Navaho mine of the Utah International Co.) using refrigerated methanol as the AGRS solvent. This paper presents a brief summary of the gasifier operation using this coal, shows examples of analyses of some of the gasifier effluent streams, and presents a summary of the results of the operation of the AGRS using the gasifier make gas as feed.

SUMMARY OF GASIFIER OPERATION

The fluidized bed gasifier and raw gas cleaning system (cyclone, venturi scrubber, filters and heat exchanger) used for these studies was originally designed for the gasification of a devolatilized coal char with a very low volatile matter content. Extensive modification of the upper part of the gasifier, the venturi scrubber system, and the heat exchanger was required for operation with the high volatile matter New Mexico coal. Table 1 shows an analysis of the char and coal used in studies to date. After modification, the system functioned well in providing a clean, dry gas to the acid gas removal system.

All of the experimental work so far has been carried out with the solid coal particles fed into the reactor several feet above the top of the fluidized bed. The particles are thus in contact with the hot product gases for several seconds before mixing into the fluidized bed, a mode of operation

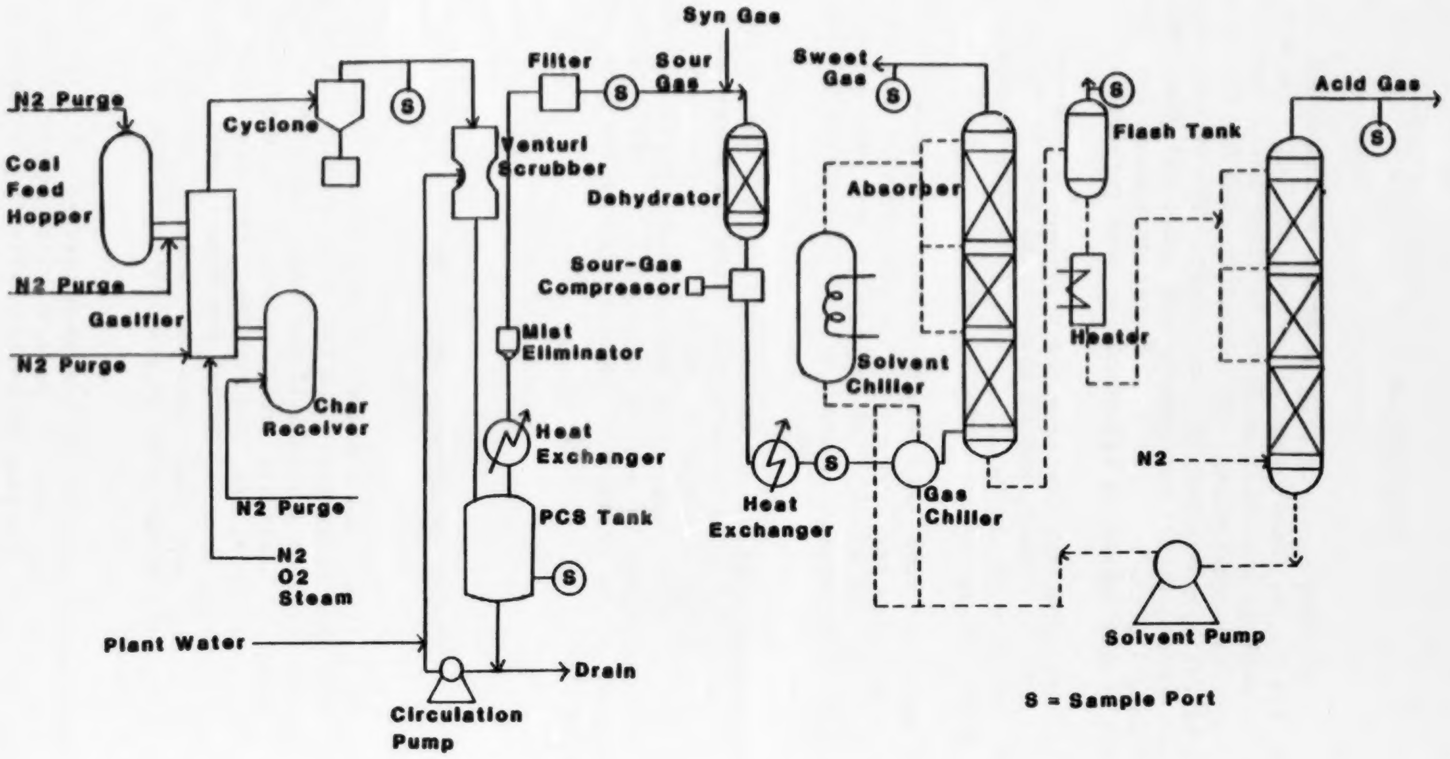
N2 Purge
Coal
Feed
Hopper
N2 Purge
Gasifier
N2 Purge
Cyclone
S
Char
Receiver
N2 Purge
N2
O2
Steam
Venturi
Scrubber
Mist
Eliminator
Heat
Exchanger
PCS Tank
S
Plant Water
Circulation
Pump
Drain
Filter
S
Syn Gas
Sour
Gas
Dehydrator
Sour-Gas
Compressor
Heat
Exchanger
S
Sweet
Gas
S
Absorber
Solvent
Chiller
Gas
Chiller
S
Flash Tank
Heater
Acid Gas
S
N2
Solvent Pump
S = Sample Port

Figure 1. Pilot Plant Facility

that tends to maximize the production of tars and other organic liquids from the coal. It is an excellent mode of operation for our present purpose since it produces relatively high concentrations of environmentally important elements and compounds.

TABLE 1
COAL AND CHAR ANALYSIS

	Coal Char	New Mexico Coal
Proximate Analysis		
Fixed Carbon	86.0	42.0
Volatile Matter	2.4	35.4
Moisture	0.9	10.5
Ash	10.7	22.6
Ultimate Analysis		
Carbon	83.8	52.5
Hydrogen	0.6	4.8
Oxygen	2.2	18.3
Nitrogen	0.1	1.2
Sulfur	2.6	0.6
Ash	10.7	22.6

A total of 15 gasifier runs were made covering a range of reactor parameters. For this series of runs, the average temperature of the fluidized bed was varied from about 1600°F to 1800°F, and the molar steam to carbon ratio was varied from about 1.0 to 2.0. The coal feed rate and the reactor pressure were kept nearly constant. Several of the first reactor runs were made with mixtures of coal and char, but all integrated runs reported on later were made with 100% coal.

At the lower temperatures the production of methane and of tars and other hydrocarbons is maximized. As the temperature is increased, the make gas rate increases, the production of methane and other hydrocarbons decreases, and the concentration of CO_2 increases. As an example, conditions and mass balances for run GO-76 are shown in Table 2.

GASIFIER MODELING RESULTS

To aid in the formulation of gasifier performance correlations, a simple model has been developed which considers the gasification process to occur in three stages: instantaneous devolatilization of coal in a zone above the fluidized bed, instantaneous combustion of carbon at the bottom of the bed, and steam-carbon gasification and water gas shift reaction in a single perfectly mixed isothermal stage. The model is significant in and of itself,

Table 2

```
*******************************************
*                                         *
* NCSU DEPARTMENT OF CHEMICAL ENGINEERING *
*                                         *
* FLUIDIZED BED COAL GASIFICATION REACTOR *
*                                         *
*******************************************

                RUN GO-76  4-28-81  13:30-16:15


     REACTOR SPECIFICATIONS                               FEED RATES AND RATIOS

PRESSURE     = 100.6 PSIG ( 794.9 KPA)               COAL        = 50.86 LB/HR (23.07 KG/HR)
TEMPERATURE  = 1711.6 DEG.F ( 933.1 DEG.C)           STEAM       = 57.37 LB/HR (26.02 KG/HR)
BED HEIGHT   = 38.0 IN. (0.97 METERS)                OXYGEN      = 12.62 LB/HR ( 5.72 KG/HR)
BED DIAMETER =  6.0 IN. (0.152 METERS)               NITROGEN    =  6.74 LB/HR ( 3.06 KG/HR)
ESTIMATED BED VOIDAGE = 0.80                         PURGE N2    = 10.33 LB/HR ( 4.69 KG/HR)
SOLIDS HOLDUP = 10.4 LB ( 4.7 KG)                    STEAM/CARBON = 1.54 MOLES STEAM/MOLE C
                                                     O2/CARBON    = 0.19 MOLES O2/MOLE C
                                                     N2/O2        = 0.61 MOLES N2/MOLE O2


                  ELEMENTAL MATERIAL BALANCES : FLOWS IN LB/HR

                  MASS      C        H        O        N        S

         COAL     50.9    24.81     2.01    11.53     0.51    0.422
        GASES     87.1     0.00     6.42    63.56    17.07    0.000
  TOTAL INPUT    137.9    24.81     8.43    75.09    17.58    0.422

         CHAR     13.3     6.10     0.12     0.00     0.07    0.074
         DUST      0.1     0.03     0.00     0.00     0.00    0.000
        GASES    121.6    18.38     8.44    76.97    17.52    0.263
   WASTEWATER      0.0     0.00     0.00     0.00     0.00    0.000
 TOTAL OUTPUT    135.0    24.51     8.56    76.98    17.59    0.337

 % RECOVERY      97.9%    98.8%   101.6%   102.5%   100.0%    80.0%


                      OUTPUT VARIABLES

          CARBON CONVERSION (PERCENT)               74.1

          DRY MAKE GAS FLOW RATE (SCFM)             19.2

          HEATING VALUE OF SWEET GAS (BTU/SCF)     373.7

          EFFLUENT FLOW RATES (LB/HR)
                         CO                         15.65
                         H2                          2.06
                         CH4                         3.40
                         CO2                        33.42
                         N2                         17.52
                         H2S                         0.271
                         COS                         0.015
```

but its particular importance to the project is that it enables the specification of gasifier conditions required to produce a feed to the acid gas removal system with a predetermined flow rate and composition.

In a previous report (Ferrell et al., 1981), the structure of the model was presented, and the ability of the model to correlate data on the gasification of a devolatilized bituminous coal was demonstrated. The model was subsequently extended to include the evolution of volatile gases in the pyrolysis stage of the gasification process, and used to fit the data from the present series of runs with the New Mexico subbituminous coal. The model takes as input the average reactor bed temperature and pressure, the bed dimensions, feed rates of coal, steam, oxygen, and nitrogen, solids holdup in the bed, and ultimate analysis of the feed coal, and calculates carbon conversion and make gas flow rate and composition. A complete description of the model in its present form will be given in an EPA report now in preparation. Plots of model predictions vs measured values of carbon conversion and dry make gas flow rate are shown in Figures 2-3. The reasonably close proximity of most points to the 45 degree line is gratifying in view of the simplicity of the model. The proximity of the points corresponding to the "best" runs (from the standpoint of satisfying mass balances) is even more satisfying.

The model also does a good job of correlating data on the evolution of individual species. Figure 4 shows predicted versus measured values of the rate of production of CO from the gasifier. Similar plots have been obtained for the production of H_2 and CO_2. The good correspondence seen in these plots suggests that the model can be used to predict the composition of the gasifier make gas for a specified set of reactor conditions, and also to study the effects of individual reactor variables on yield.

AGRS OPERATION AND RESULTS

As previously mentioned, top feeding coal into the gasifier allows a substantial amount of devolatilization to take place before the coal enters the fluidized bed. While most commercial fluidized bed gasifiers will use a deep-bed injection method of feeding coal into the fluidized bed, it was decided not to modify our system in order to maximize the formation of tars, oils, and other hydrocarbons and to provide a more complete test of the AGRS.

It should also be noted that the relatively simple acid gas removal system used in this study lacks the complexity of the selective systems found in many physical absorption processes. These systems, which use more than one absorber and stripper, and often several flash tanks, separate sulfur gases from carbon dioxide before further processing of the acid gas. This is done to concentrate the sulfur gases before they are fed to a sulfur recovery unit, and to recover the CO_2 or vent the CO_2-rich stream to the atmosphere. While the AGRS used in this study could have been modified to emulate an

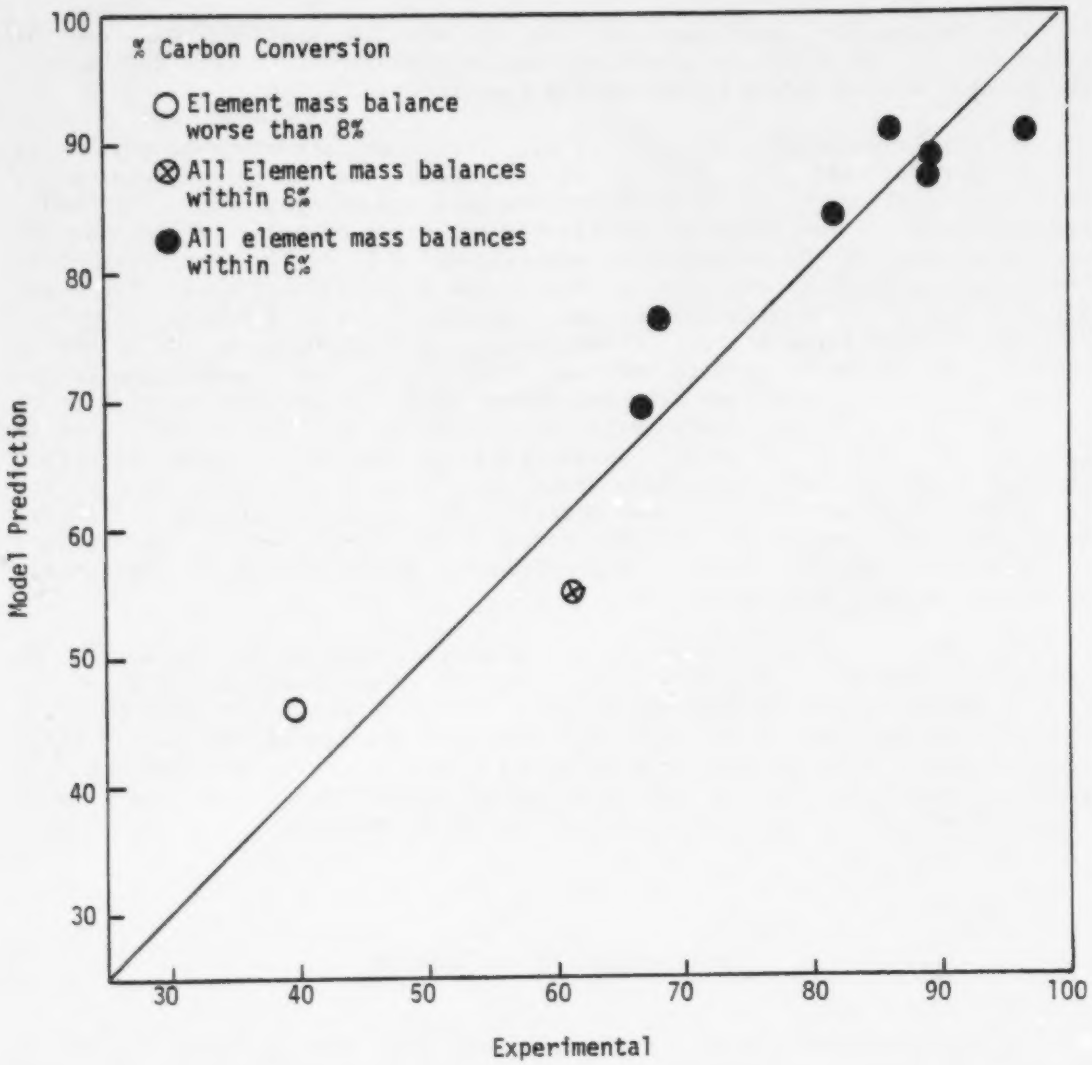

Figure 2. Predicted vs. Experimental Carbon Conversion, Gasification of New Mexico Coal

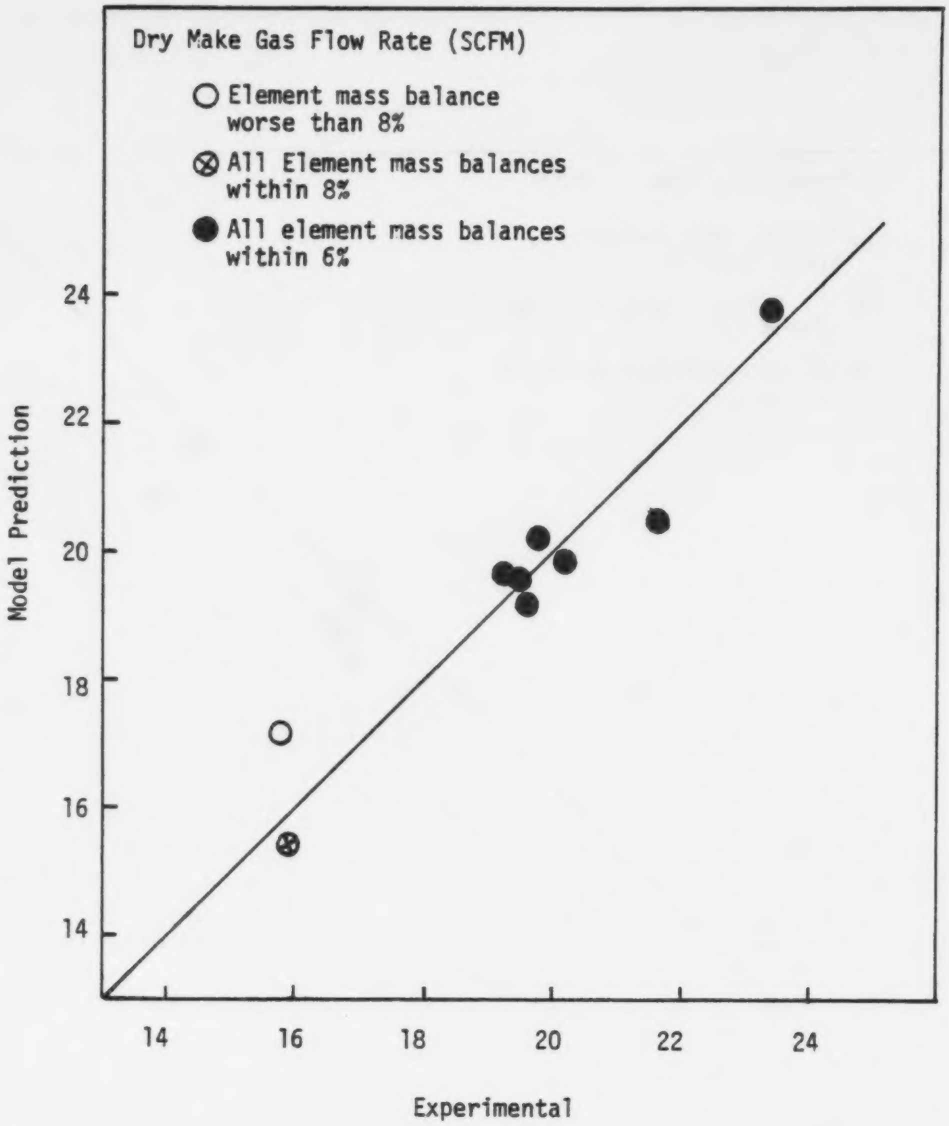

Figure 3. Predicted vs. Experimental Dry Make Gas Flow Rate, Gasification of New Mexico Coal

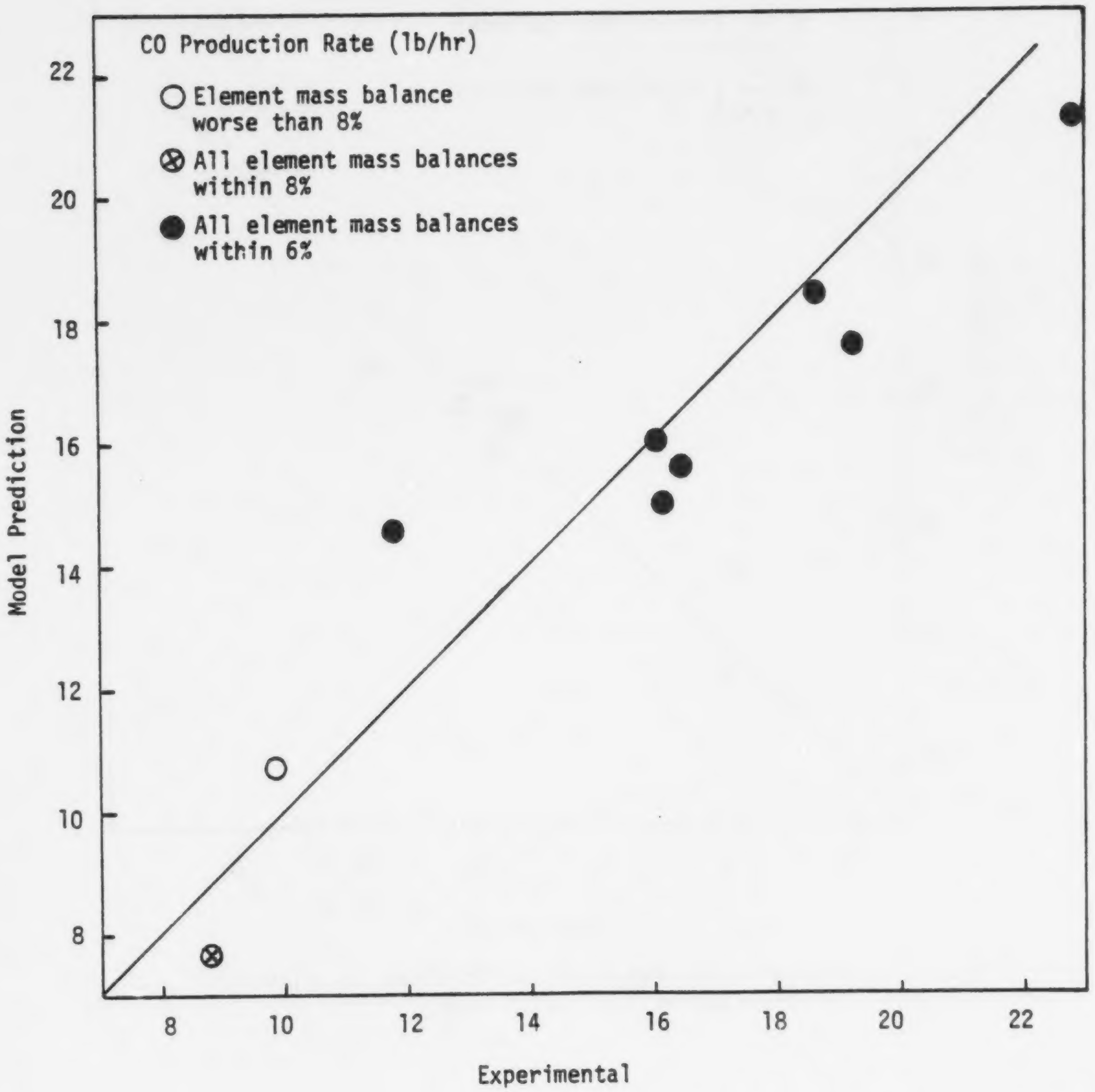

Figure 4. Predicted vs. Experimental Production Rate of CO from Gasification of New Mexico Coal

existing selective absorption process, it was decided that data obtained from a relatively simple but well-characterized system would be of more use than data obtained from a fairly complex system, similar but not identical, to existing commercial systems. Through judicious use of computer simulation and engineering calculations, the data obtained from our system should be extrapolatable to more industrially significant situations.

EXPERIMENTAL PROGRAM

In designing the experimental program to be used in these studies, the use of a full factorial experimental design was not believed to be necessary. The program was designed to cover the broadest range of operating conditions possible for the system of New Mexico coal and refrigerated methanol. Effects of variations in important process variables were examined by comparing all runs to a base case. Although this approach is not exhaustive, it provides a framework with which to examine the environmental consequences of acid gas removal with methanol. In addition, the work done in this study will be useful in developing experimental programs for other coals and acid gas removal solvents to be studied in our facility.

Table 3 shows the operating conditions used for the nine runs made in this part of the study. Also shown are inlet and outlet gas concentrations for the major acid gases in the absorber.

DISCUSSION

From an environmental perspective, operation of the acid gas removal system in a coal gasification process becomes important when harmful compounds or pollutants may be discharged to the atmosphere. Although there are a wide variety of extremely toxic materials released from coal during gasification, as long as they remain within the gas cleaning system or are properly processed, they pose little problem. However, while these harmful materials are seldom purposely discharged to the atmosphere from the acid gas removal system under normal operating conditions, several of the AGRS gas streams are fed to downstream processes. There, inability to handle toxic compounds and pollutants may result in their discharge to the atmosphere. It is therefore important to know what compounds enter the AGRS, and how they distribute in the system under various processing conditions.

Of the runs shown in Table 3, run GO-76, AMI-57 will be used to illustrate AGRS performance results. Gas analyses from the six different locations shown in Figure 1 are given in Table 4.

TABLE 3
OPERATING CONDITIONS FOR COAL GASIFICATION RUNS

Run Number AMI-	43	44	45	47	52	53	57	59	60
GO-	68B	69B	70	71B	72	73B	76	78	79
Absorber									
Pressure Atm	18.0	18.0	31.6	31.6	31.6	18.0	31.6	18.0	24.8
Packing Height Ft	7.1	7.1	7.1	7.1	21.3	7.1	7.1	7.1	7.1
Inlet Liquid Flow	63.6	63.5	129.3	130.5	127.9	127.5	61.7	127.3	100.8
Inlet Solvent Temp	-36.1	0.8	-36.3	-34.9	-35.7	-5.4	-36.2	-3.5	-21.0
Inlet Gas Flow	18.1	17.0	17.1	16.8	16.8	17.9	15.4	14.9	16.0
Inlet Gas Temp F	40.1	47.6	22.3	36.3	38.1	42.5	50.4	44.2	56.4
H_2S in ppm	2950	2900	2550	4682	3023	1710	2868	3180	2139
H_2S out ppm	220	280	260	151	105	172	48	190	260
COS in ppm	119	112	79	133	67	60	76	81	84
COS out ppm	12	10	5	7	6	7	1	4	19
CO_2 in %	20	22	21	22	23	22	22	23	22
CO_2 out %	--	1	3	--	--	--	--	--	--
Flash Tank									
Pressure Atm	4.2	10.9	11.0	11.0	11.0	10.8	11.0	10.8	10.7
Stripper									
Pressure Atm	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
Packing Height Ft	21.3	21.3	21.3	21.3	21.3	21.3	21.3	21.3	21.3
Stripping N_2 Flow	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3
Inlet Gas Flow	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0
Inlet Solvent Temp F	8.4	14.6	-5.6	48.0	48.0	48.1	48.1	48.1	37.6
Overall Mass Balance Closure									
Gasifier %	98.0	96.6	95.3	103.5	98.6	97.8	97.9	98.3	100.6
AGRS %	103.8	102.3	103.0	104.8	101.4	103.1	99.2	101.8	95.5

All Flows in lb-mole/hr-ft^2

The sample train sample is taken downstream from the cyclone separator and is the closest sampling point to the gasifier. Unreacted steam in the gas is first condensed and removed before the sample is taken. The PCS tank sample is taken after the gas quenching step but before the dehydrating towers and sour gas compressor. The sour gas sample is taken after the PCS tank and after the gas has been dehydrated, compressed, and cooled to remove the heat of compression. The high levels of several hydrocarbon and sulfur species in the sour gas sample may be attributed to the presence of condensate in the gas sampling lines. A trap located near this sampling station accumulated small amounts of a condensed hydrocarbon phase which was analyzed by GC/MS after run AMI-60. It is thought that this sample provides qualitative information on the variety of trace compounds entering the AGRS.

When the system is operating at steady state, the compositions of the sample train, PCS tank and sour gas samples will be nearly the same. This is some indication of the quality of the run. More detailed descriptions of the sampling and analytical procedures can be found in Ferrell et al. (1981).

TABLE 4
GAS ANALYSIS SUMMARY FOR AMI-57/GO-76

Species	Sample Train	PCS Tank	Sour Gas	Sweet Gas	Flash Gas	Acid Gas
H_2	31.60	31.11	31.29	42.38	15.58	0.00
CO_2	23.51	23.91	21.98	-----	25.99	64.74
C_2H_4	0.52	0.53	0.56	0.0242	1.28	1.54
C_2H_6	0.72	0.72	0.76	0.0164	1.92	2.13
H_2S	0.250	0.284	0.287	0.0048	0.090	0.66
COS	0.0078	0.0076	0.0076	0.0001	0.0041	0.027
N_2	19.36	19.61	19.93	26.79	19.27	23.06
CH_4	6.56	6.46	6.57	7.54	14.20	2.36
CO	17.29	17.47	17.92	23.35	21.55	1.80
Benzene	0.087	0.097	0.234	TRACE	0.0031	0.15
Toluene	0.031	0.034	0.534	0.0054	0.0033	0.030
Ethyl Benz.	0.0016	0.0017	0.0450	-----	-----	-----
Xylenes	0.0080	0.0094	0.1557	-----	-----	-----
Thiophene*	44	44	127	-----	-----	-----
CH_3SH*	16	29	28	TRACE	5	TRACE
C_2H_5SH*	TRACE	-----	8	-----	-----	-----
CS_2*	TRACE	3	TRACE	TRACE	TRACE	TRACE
Propylene*	1505	1521	1811	107	995	4640
Propane*	208	198	253	301	172	2203
Butane*	185	150	143	54	91	71
Methanol**	-----	-----	-----	-----	-----	3.68

*Parts per Million (volume) **Estimated

Acid Gas Removal

The primary function of the AGRS is to remove CO_2 and sulfur compounds from the gases produced during coal gasification. When using refrigerated methanol, the absorber also acts as an excellent trap for any other compound which condenses or disolves in the methanol at absorber conditions. Table 3 shows the concentrations of H_2S, COS and CO_2 for the nine coal gasification runs. Using AMI-47 as the base case, the effect of process conditions on acid gas removal can be seen.

Because the acid gas content of the solvent entering the absorber has a pronounced effect on removal efficiencies, ineffective solvent regeneration in the stripper can be a problem. In run AMI-45, the stripper was operated at -5.6°F rather than at 48°F as in AMI-47. Comparing the results from AMI-47 and AMI-45, the former shows a significantly better acid gas removal efficiency as a result of the higher operating temperature in the stripper.

The effect of packing height on removal efficiency can be seen by comparing AMI-47 with AMI-52. In AMI-52, 14.2 feet of additional packing was used with only a marginal improvement in the outlet H_2S levels. The acid gas removal efficiencies for the two runs are almost the same.

From the results of these three runs and the other runs in Table 3, it appears that for the range of conditions studied here, the most significant factor in high acid gas removal efficiencies is stripping efficiency. With the use of more extreme operating conditions and "cleaner" methanol fed to the absorber, the levels of CO_2, COS and H_2S in the sweet gas can be reduced to acceptable levels. This is a particularly important point in the case of COS removal which poses problems for many coal gas cleaning systems. From the data collected in this study, it appears that refrigerated methanol is effective in removing COS and no unusual solubility characteristics were evident at moderate pressures and low liquid temperatures.

Trace Sulfur Compounds

There are also several other sulfur compounds besides H_2S and COS present in the gas fed to the AGRS which must be removed. Table 4 shows the distribution of several of these compounds in the AGRS. While there is some scatter in the analyses for methyl mercaptan, thiophene, CS_2, and ethyl mercaptan/dimethyl sulfide, it appears that in most runs they are removed to very low levels in the absorber.

A point of potential environmental significance is that while these compounds are removed to low levels, they are not completely accounted for in the flash and acid gas streams. This can be seen for methyl mercaptan and thiophene, which are present in relatively high levels in the feed gas. These compounds will accumulate in the recirculatory solvent and most likely eventually leave the system in one of three exit streams: sweet gas, flash gas, or acid gas. Because most sulfur recovery systems cannot treat mercaptans and thiophene, they will present emission problems if some additional method of treating these gases is not used. This can be a significant problem because the total sulfur from mercaptans, organic sulfides, CS_2, and thiophene is approximately half of the total sulfur associated with COS. If these compounds appear with the sweet gas, they are likely to affect adversely downstream methanation catalysts. The presence of these compounds in the sweet gas stream is also a problem if the gas is to be burned for immediate use because the sulfur in these compounds will be converted to SO_2.

In examining the results from all runs, there appears to be some pattern of trace sulfur species distribution. The increase in stripper temperature from the low levels of AMI-45 to 48°F for AMI-47 resulted in substantially greater amounts of mercaptan and thiophene in the acid gas stream. The results from AMI-44, which represents the "worst case" for absorber performance, show an increase in mercaptan levels in the sweet gas. Apparently, the conditions used in the absorber for this run were not sufficient to remove the mercaptans to low levels. CS_2 seems to distribute to all exit streams in most of the runs despite the differences in process conditions.

Perhaps the most significant finding here is that over a wide range of processing conditions, the presence of at least small amounts of several different sulfur species is to be expected in all AGRS exit streams, and provision must be made for handling the associated problems.

Aliphatic Hydrocarbons

As the amount of volatile matter present in a particular coal increases, the production of aliphatic, aromatic, and polynuclear aromatic compounds produced during gasification also increases. Over the range of conditions studied here, the most significant point to be made about the distribution of aliphatic hydrocarbons is their presence in significant quantities in the flash and acid gases. Although flashing of the methanol down to atmospheric pressure prior to stripping would release most of the hydrocarbons, the CO_2-rich flash gas would still contain substantial amounts of several hydrocarbon species. This stream would require further processing before it could be vented.

In run AMI-57, in which the gasifier was operated at a lower temperature to increase the production of hydrocarbons, the aliphatics (excluding methane) make up almost 4.5% of the acid gas stream and 3.5% of the flash gas stream. While staging the flashing operations may result in a better distribution of these compounds, the total product from the flashing and stripping operations must be either recovered as product, fed to a sulfur recovery unit, or vented to the atmosphere. Since it is unlikely that all of the aliphatic hydrocarbons will appear in the sweet gas stream, as evidenced by the data collected here, additional treatment will be necessary to prevent their eventual appearance in a vent stream.

There appears to be no unusual pattern of distribution of aliphatic hydrocarbons in the AGRS. The lighter hydrocarbons-- methane, ethylene, and ethane-- seem to distribute as would be indicated from an examination of their pure-component solubilities in methanol. The magnitude of their solubilities, however, are greater than would be expected from Henry's law, especially at the high pressures used in the absorber. This is evident from the lower than predicted levels of ethane and ethylene in the sweet gas in several of the runs.

Aromatic Hydrocarbons

Because large amounts of aromatic hydrocarbons are produced during coal gasification, the potential for environmental problems is great. These compounds, which range from benzene to polynuclear species of many forms, must be prevented from escaping from the gas cleaning process and their distribution throughout the gas cleaning system is of great concern.

Table 3 summarizes the information obtained from a single run. The simpler aromatics, benzene, toluene, and xylene, typically make up 0.1% (by volume) of the gas stream entering the AGRS.

Analyses performed for selected runs indicate that significant quantities of these compounds are found in the solvent leaving the stripper. Results from two runs are reported in Table 5. These compounds will build up in the solvent to the point of saturation. If the solvent is not effectively purged of these compounds periodically, they will begin to appear in several of the process streams.

TABLE 5
METHANOL ANALYSIS FOR STRIPPER EXIT
ALL ANALYSES REPORTED IN PPM (VOLUME)

	AMI-44/GO-69B	AMI-57/GO-76
Benzene	190	157
Toluene	200	196
Ethylbenzene	30	87
Xylenes	70	203

Methanol Analysis

In order to identify the various hydrocarbon species that accumulate in the methanol, samples of the methanol leaving the stripper were taken for several runs. These samples were then analyzed by gas chromatography/mass spectrometry.

Initial samples taken of the stripped methanol were analyzed by the Research Triangle Institute, Research Triangle Park, North Carolina. The results from AMI-44/GO-69B and AMI-57/GO-76 are shown in Figures 5 and 6 and in Tables 6 and 7. The gasifier conditions for AMI-57/GO-76 were designed to result in the production of larger amounts of heavy organics and tar than the other runs made in this study. The spectra from Figures 5 and 6 show that this result was achieved. The presence of several siloxanes and phthalates were probably related to some contamination of the sample during processing.

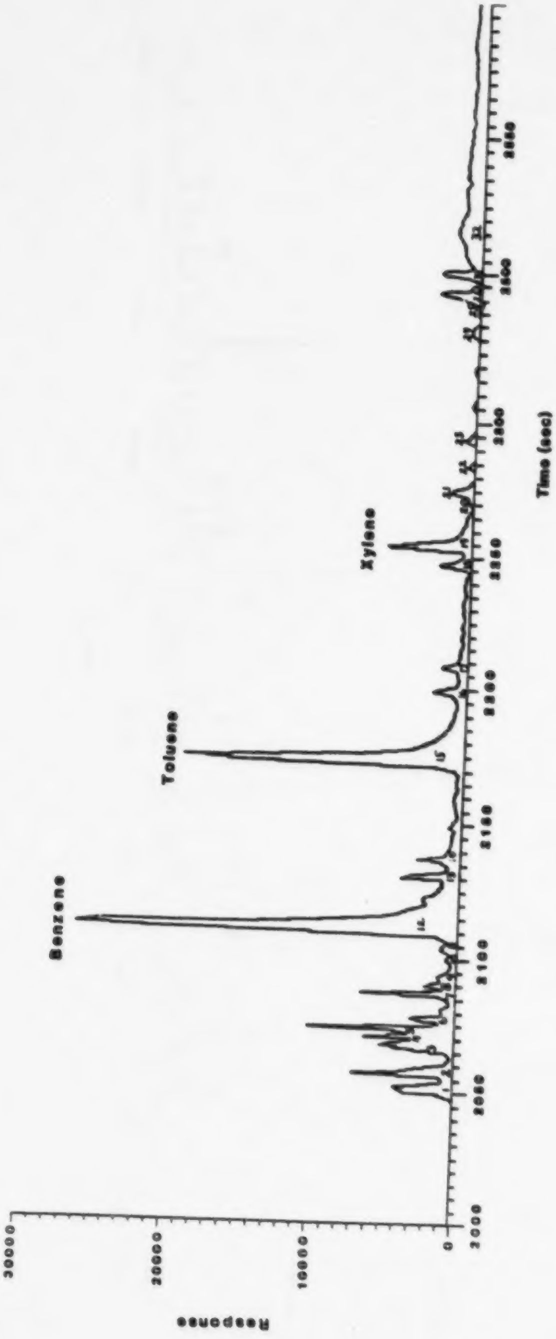

Figure 5. Analysis of Stripper Exit Methanol from AMI-44/GO-69B

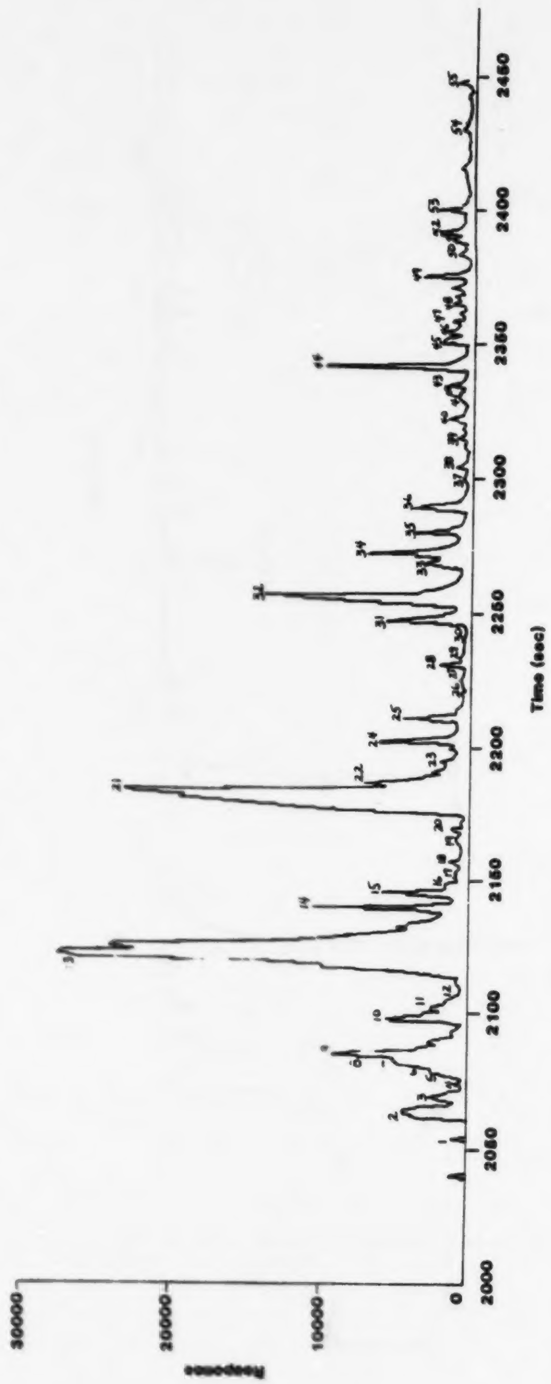

Figure 6. RTI Analysis of Methanol at Stripper Exit

Results from these runs indicate that most of the compounds accumulating in the methanol are simple aromatics, primarily substituted benzenes. A few C_{10} and C_{11} isomers were identified, indicating that napthalene is probably present but at trace levels. The presence of trace amounts of C_{14} and C_{15} isomers were found in AMI-57 but they could not be better identified. These may be polynuclear aromatics but they were present in very small amounts relative to the simpler aromatics.

Later in the sampling program, samples from AMI-60/GO-79 were analyzed by the GC/MS facility at North Carolina State University. The results from these analyses are shown in Figures 7 and 8. These Figures show the mass spectra for the stripped methanol before and after the run. Although compound identification was not performed for these analyses, comparison of the two spectra shows the relative changes in the levels of hydrocarbons. This methanol had been used for several previous runs and had accumulated significant quantities of a variety of organics. The spectra for the sample taken at the end of the run show that the locations of most peaks have not changed but the relative sizes of several peaks have. This indicates that these hydrocarbons were in fact, accumulating and will continue to do so until they saturate the solvent.

TABLE 6
STRIPPER EXIT METHANOL FOR AMI-44/GO-69B

Peak Number from Figure 5	
1.	CO_2
2.	butene isomer
3.	pentene isomer
4.	2-methyl-2-butene
5.	cyclopentadiene
6.	cyclopentene
7.	C_6H_{12} isomer
8.	C_6H_{14} isomer
9.	C_6H_{10} isomer
10.	methyl cyclopentane
11.	methyl cyclopentadiene
12.	benzene
13.	C_7H_{14} isomer
14.	C_7H_{16} isomer
15.	toluene
16.	C_8H_{16} isomer
17.	C_8H_{18} isomer
19.	ethyl benzene
20.	xylene (M,P)
21.	styrene
22.	xylene (O)
23.	C_9H_{18} isomer
24.	C_9H_{20} isomer
25.	$C_{10}H_{20}$ isomer
26.	$C_{10}H_{22}$ isomer
27.	$C_{10}H_{22}$ isomer
28.	-----------
29.	$C_{11}H_{24}$
30.	methyl undecane
31.	$C_{11}H_{24}$ isomer
32.	Sat'd hydrocarbon
33.	phthalate
34.	Sat'd hydrocarbon

Samples of liquid condensing in the knockout tank downstream from the sour gas compressor were collected and analyzed by GC/MS. This condensate contains most of the heavier hydrocarbons fed to the AGRS. Results of these analyses are presented in Figure 9 and Table 8, and show that the compounds identified are very similar to those found in the stripped methanol from AMI-44 and AMI-57. Again, mostly simple aromatics were found. No polynuclear aromatics were present, which supports the findings of the earlier analyses.

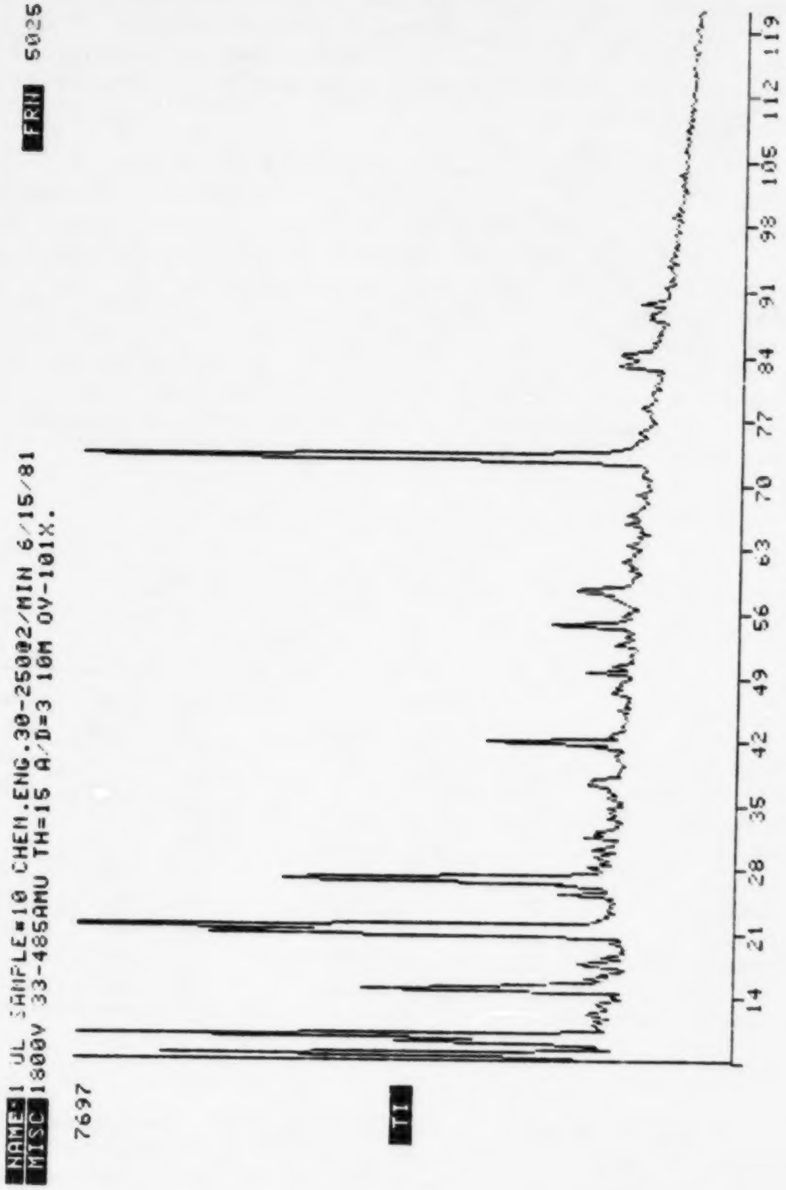

Figure 7. Stripper Exit Methanol Before Integration for AMI-60

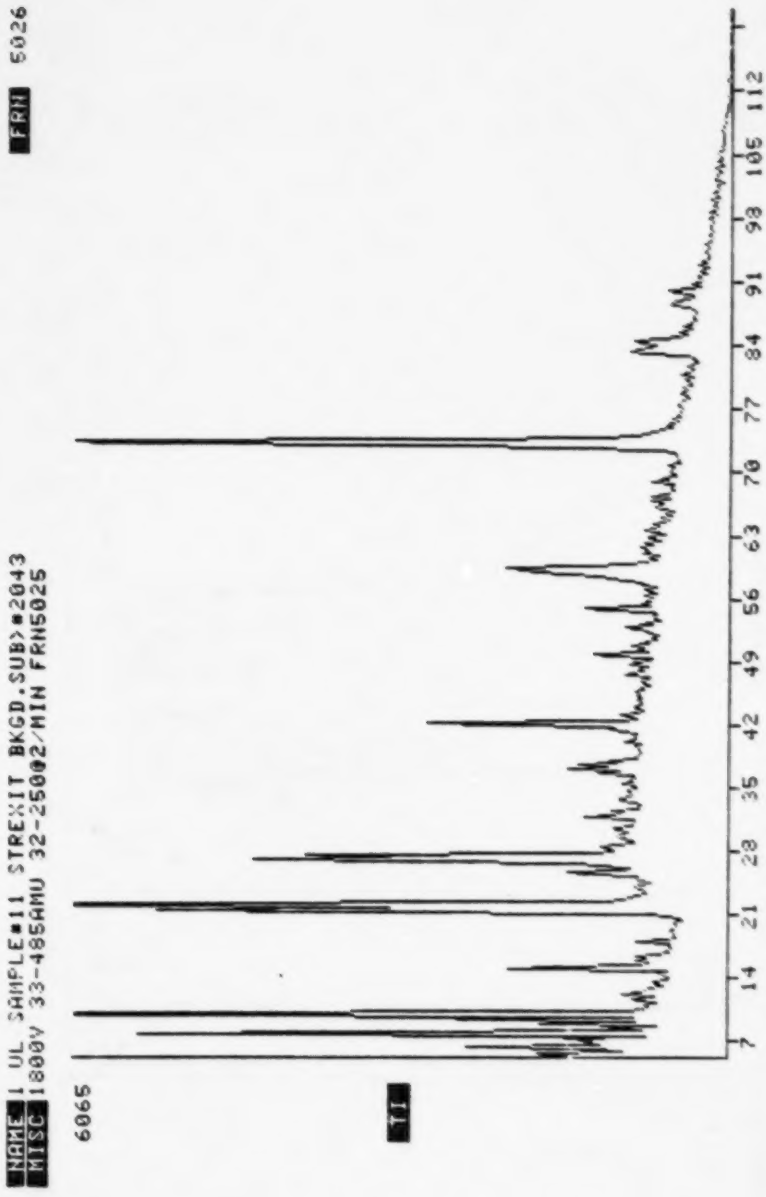

Figure 8. Stripper Exit Methanol Taken at the End of AMI-60

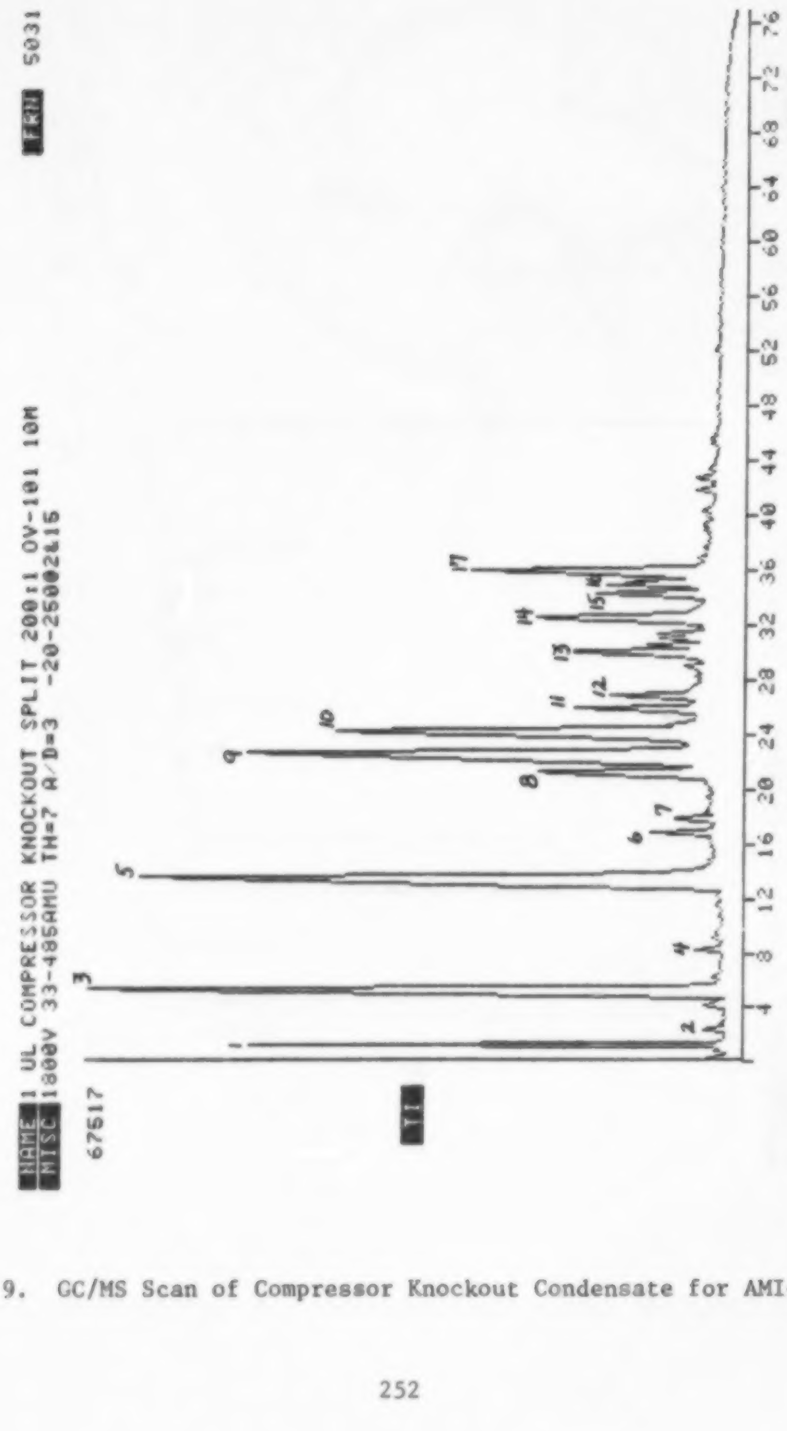

Figure 9. GC/MS Scan of Compressor Knockout Condensate for AMI-60

TABLE 7
AMI-57/GO-76 STRIPPER EXIT METHANOL

Peak Number from Figure 6

1. sat'd hydrocarbon
2. CO_2
3. C_4H_8 isomer
4. tetramethylsilane
5. trichlorofluromethane
6. C_5H_{10} isomer
7. unknown
8. Freon 113
9. cyclopentadiene
10. C_6H_{12} isomer
11. C_6H_{14} isomer
12. C_6H_{10} isomer
13. benzene
14. C_7H_{14} isomer
15. C_7H_{16} isomer
16. C_7H_{16} isomer
17. C_7H_{12} isomer
18. C_7H_{12} isomer
19. C_7H_{12} isomer
20. unknown hydrocarbon
21. toluene
22. methyl thiophene isomer
23. C_8H_{16} isomer
24. C_8H_{16} isomer
25. C_8H_{16} isomer
26. C_8H_{16} isomer (trace)
27. C_8H_{14} isomer (trace)
28. hexamethyl cyclotrisiloxane
29. C_9H_{20} isomer
30. C_9H_{18} isomer
31. ethyl benzene
32. xylene (M,P)
33. styrene
34. xylene (O)
35. C_9H_{18} isomer
36. C_9H_{20} isomer
37. C_3 alkyl benzene
38. $C_{10}H_{22}$ isomer
39. unknown hydrocarbon
40. unknown hydrocarbon
41. $C_{11}H_{24}$ isomer
42. C_3 alkyl benzene
43. C_3 alkyl benzene
44. $C_{10}H_{22}$ isomer
45. $C_{10}H_{22}$ isomer
46. C_4 alkyl benzene
47. $C_{10}H_{22}$ isomer
48. $C_{10}H_{20}$ isomer
49. unknown hydrocarbon
50. C_9H_{10}
51. C_9H_8 isomer
52. alkyl benzene isomer
53. $C_1 1H_2 4$ isomer
54. $C_8H_{10}O$ isomer
55. $C_{11}H_{24}$ isomer
56. C_8H_{100} isomer
57. unknown siloxane
58. unknown siloxane
59. unknown siloxane
60. $C_{14}H_{30}$ isomer
61. $C_{14}H_{30}$ isomer
62. unknown
63. $C_{15}H_{32}$ isomer

TABLE 8
COMPRESSOR KNOCKOUT SAMPLE FROM AMI-60/GO-79
PEAK NUMBER FROM FIGURE 9

1. 1-pentene
2. hydrocarbon
3. benzene
4. hydrocarbon
5. Toluene
6. cyclo C4-C5
7. hydrocarbon
8. ethyl benzene
9. dimethyl benzene
10. substituted benzene
11. C_8 hydrocarbon
12. C_9 hydrocarbon
13. propyl or ethyl methyl substituted benzene
14. propyl or ethyl methyl substituted benzene
15. 1-decene
16. 2-propyl benzene
17. 1-ethyl-4-methyl benzene

Results from these analyses indicate that very little, if any, polynuclear aromatic compounds were present in the gas fed to the AGRS. This is a particularly important finding. Analyses of the water used to quench the gasifier product gas stream showed that a substantial amount of polynuclear aromatics were present. Evidently, scrubbing of the raw product gas with water effectively removes these compounds.

Although polynuclear aromatics are removed by the quenching process, substantial amounts of simpler aromatics will be present in the sour gas fed to the AGRS. The use of cold traps may remove some of these compounds but provision must be made to prevent their release to the atmosphere through vent streams or through the sulfur recovery unit. The accumulation of these compounds in the methanol further complicates the problem because of the increased likelihood of their distribution to a number of process streams. Achievine efficient solvent regeneration is, therefore, a key step in avoiding environmental problems.

SUMMARY

A cyclone, a cold water quench scrubber, and a refrigerated methanol absorber have been used to clean the make gas from the steam-oxygen gasification of a New Mexico subbituminous coal in a pilot-scale fluidized bed ractor. A model developed for the gasifier provides the capability of predicting the make gas amount and composition as a function of gasifier operating conditions. The methanol functioned effectively for acid gas removal. Removal of CO_2, COS, and H_2S to sufficiently low levels was achieved with proper choice of operating conditions and effective solvent regeneration.

The presence of several trace sulfur compounds--mercaptans, thiophenes, organic sulfides, and CS_2--complicates the gas cleaning process because these compounds were found to distribute among all exit streams from the AGRS. Since no provision is made to specifically treat these forms of sulfur, the possibility of their emission into the atmosphere exists and must be dealt with to avoid significant environmental problems.

A wide variety of aliphatic and aromatic hydrocarbons are present in the gas stream fed to the AGRS. The aliphatic hydrocarbons, ranging from methane to butane, cover a wide range of solubilities. Their presence in all AGRS streams must be anticipated to prevent their emission to the atmosphere.

While a wide range of simple aromatics were identified in the gas stream fed to the AGRS, essentially no polynuclear aromatic compounds were found. Apparently, the water quenching process effectively removes these compounds from the gasifier product gas. However, significant quantities of simple aromatics were found to accumulate in the recirculating methanol, indicating a potential for their eventual discharge to the atmosphere. Provision must be made to periodically purge the solvent of these compounds and/or remove them prior to the AGRS through cold traps.

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ADVANCED TECHNIQUES FOR FLUE GAS DESULFURIZATION†

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ABSTRACT

In 1979 the combustion of sulfur-bearing fuels accounted for more than 80 percent of the SO_2 emissions in the United States. These emissions can be controlled to a degree by burning low-sulfur fuels or by pretreating the fuel to lower its sulfur content. Currently the most widely-practiced technological control involves scrubbing the combustion flue gases to remove the SO_2. Flue gas desulfurization systems can be categorized as nonregenerable or "throwaway" and regenerable or producing a saleable product. Several systems in each category will be discussed as to their advantages and disadvantages. In addition, several recent developments regarding waste disposal and enhanced SO_2 removal will be presented.

INTRODUCTION

Sulfur dioxide (SO_2) is one of a number of sulfur-containing pollutants found in the atmosphere. It enters the air primarily from the combustion of coal and oil, but also from various other industrial processes. The combustion of sulfur-containing fuels accounts for more than 80 percent of the SO_2 emissions in the United States(1,2). These emissions can be controlled to a degree by burning low-sulfur fuels or by pretreating the fuel to lower its sulfur content. Currently the most effective control involves scrubbing the combustion flue gases to remove SO_2 by flue gas desulfurization (FGD) technology.

This paper briefly discusses methods for controlling these emissions, related waste disposal, and process costs. Since most FGD technology has been developed in relation to coal-fired steam electric generating plants, the major emphasis will be advanced FGD systems for these plants. Such systems, however, are being used at industrial sites and may be adaptable to commercial gasification facilities. Sulfur oxides (SO_x) are pollutants of major environmental concern, and their formation in power generation units of commercial medium- and high-Btu gasification plants may be at levels requiring control. Several proposed gasification plants include FGD systems on coal-fired power generation units for these plants.

While SO_x are not the major pollutant in raw product gases from coal gasifiers, commercial processes for cleaning these gases or upgrading the quality of the synthetic gas produced may produce SO_x at levels requiring control to meet air quality constraints. For example, the production of sulfur from sulfur compounds in raw product gases can lead to tail gases containing reduced levels of sulfur compounds and other combustible gases. Combustion of the tail gases along with coal in the power-producing component of a medium- or high-Btu gasification plant may generate SO_x at levels requiring FGD, but would reduce fuel requirements through combustion of the tail gases. Thus the integrated control of SO_x in flue gases from the incineration of pollutant-bearing tail gases and the combustion of coal in connection with power or steam production may be more cost effective than treating separate pollutant streams.

FGD systems are classified into two categories: nonregenerable or "throw-away" systems and regenerable systems which produce a saleable product. They may be further classified into wet and dry FGD systems, the distinction being that saturated (with water) and unsaturated flue gas, respectively, result from the gas cleaning process. A brief discussion of these categories of advanced FGD systems will now be presented.

NONREGENERABLE FGD SYSTEMS

Presently, nonregenerable FGD systems can be classified into two types, wet and dry. Each type of process will be discussed.

Most commercial wet FGD systems, that are either operating or planned for use in utility applications, are lime or limestone based systems. The major driving force for using these "throwaway" systems rather than regenerable FGD technology is one of economics. Wet limestone systems are slightly more economical than wet lime systems because of the cost and energy requirements associated with calcination of the limestone to produce lime. This cost difference is expected to increase with rising energy costs. Although these calcium-based systems are in wide use, their performance to date has been limited by reagent reactivity which results in low soluble alkalinity, relatively higher liquid-to-gas (L/G) ratio requirements, and larger reaction tanks than other FGD processes.

Wet Lime/Limestone(3)

Wet lime/limestone FGD processes (Figure 1) employ a scrubbing slurry of lime or limestone to remove SO_2. As a side benefit, these processes can also be designed to remove fly ash and chlorides simultaneously. Because lime/limestone processes are nonregenerable, they produce large quantities of waste solids. This characteristic could place them at a disadvantage compared with regenerable processes where disposal costs are high. Regenerable processes, however, still require disposal of waste fly ash and chlorides by environmentally acceptable methods, and these waste products can amount to more than 50 percent (high ash fuels) of the volume of solid waste produced by lime/limestone processes.

Lime/limestone systems are usually less complex than regenerable systems, and they generally cost less to install and operate than other wet FGD processes. Consequently, lime/limestone FGD processes are the most widely used wet FGD systems in operation.

Lime/limestone FGD processes consist of four steps:

1. Feed material processing.
2. Absorption.
3. Solids precipitation.
4. Solids concentration and disposal.

Flue gas enters the absorber (Figure 1) where it contacts the circulating scrubbing slurry containing calcium ions from dissolved lime or limestone. SO_2, fly ash, and chlorides contained in the flue gas are removed by the

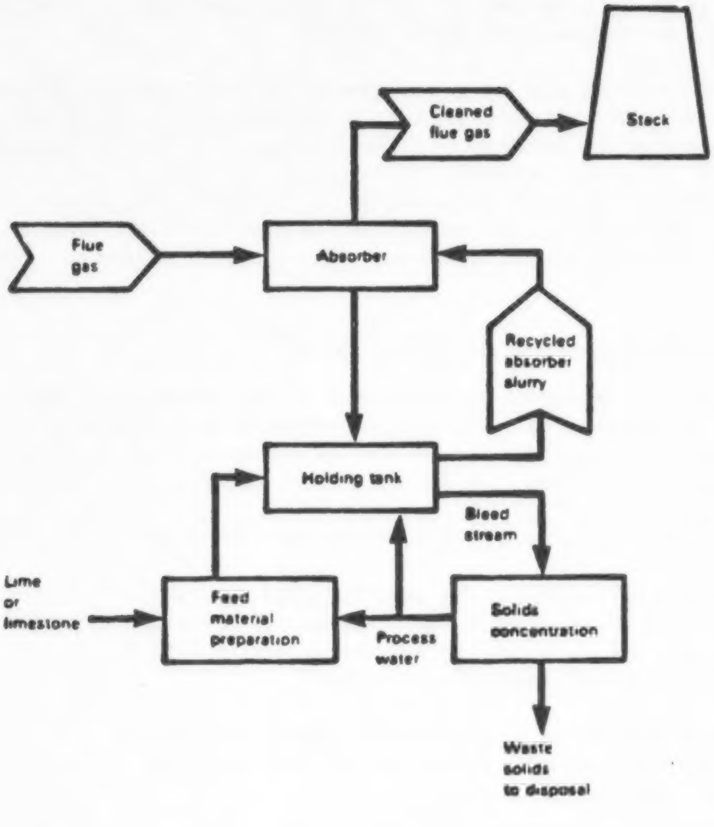
Cleaned flue gas
Stack
Flue gas
Absorber
Recycled absorber slurry
Holding tank
Bleed stream
Lime or limestone
Feed material preparation
Process water
Solids concentration
Waste solids to disposal

Figure 1. Typical Lime/Limestone FGD Process Flow(3)

circulating slurry. Alkaline species in the liquor neutralize the absorbed SO_2, promoting the formation of ions of sulfite and sulfate. Water droplets are removed from the cleaned flue gas by mist eliminators as they leave the absorber. The clean, water-saturated, flue gas is reheated, if necessary, to counter material corrosion and/or plume dispersion problems and then is exhausted through the stack to the atmosphere.

The scrubbing slurry, which may be supersaturated with solids of calcium sulfite and calcium sulfate, flows to an effluent holding tank or precipitation vessel. In the holding tank, fresh makeup lime or limestone is added, and reaction products are precipitated. One effluent stream from the holding tank is recycled to the absorber; another is bled off for concentration and disposal of waste solids.

Solids in the bleed stream may be concentrated in a thickener, filter, or centrifuge, or may be sent directly to a holding/settling pond. Clarified process water is returned to the system. Concentrated solids may be disposed of in ponds or used for landfill and may or may not be chemically stabilized. It is also possible to convert the solids to gypsum for use in portland cement or wallboard manufacture. This, however, requires the additional process operations of oxidation and purification.

Wet Lime/Limestone with Adipic Acid Enhancement(4)

IERL-RTP has sponsored extensive laboratory, pilot, prototype, and commercial scale studies on an adipic acid enhanced wet limestone system which shows significant improvement in operation over non-adipic acid enhanced wet limestone systems. Addition of relatively small quantities of adipic acid (approximately 1500 ppm), in either conventional or forced oxidation limestone FGD systems, provides these important benefits:

- Significantly enhanced SO_2 removal efficiency in either conventional or forced oxidation modes (compared with additives such as MgO which may be of little benefit in forced oxidation systems).

- Increased limestone utilization; hence, decreased waste solids disposal requirements and improved scrubber reliability.

- Lower projected capital and operating costs than conventional limestone FGD systems.

- Not adversely affected by chloride as is the limestone/MgO process; thus, it is especially attractive for closed-loop operation.

- Less expensive and less energy intensive limestone rather than lime is used.

Adipic acid is a weak dicarboxylic acid which buffers the slurry pH and thus enhances the SO_2 solubility and limestone dissolution rate. An important advantage of adipic acid as compared with other scrubber additives is that its ability to improve SO_2 removal is not affected by chlorides. Adipic acid significantly enhances SO_2 removal over a range of operating conditions (with scrubber slurry pH's of 5.0 to 5.5). Operation at the lower end of the typical pH range increases limestone utilization and may reduce scaling and mist eliminator fouling. Improved limestone utilization in turn reduces both the amount of limestone required and the quantity of solid wastes produced by the FGD system. These improvements represent an estimated 6 percent reduction in capital investment and 7 percent reduction in operating costs.

Figure 2 shows enhanced SO_2 removal due to adipic acid addition. For example, a scrubber feed with a pH of 5.5 and an adipic acid concentration of approximately 1600 ppm resulted in 95 percent SO_2 removal, as opposed to 70 percent SO_2 removal at the same operating conditions without adipic acid. Adipic acid addition also improved limestone utilization, increasing it to over 90 percent.

Research and development activities have focused on adipic acid to enhance the performance of the limestone FGD process. However, other organic acids will also enhance the process. One of the most intriguing alternatives is dibasic acid (DBA) material which is a by-product of the adipic acid manufacturing process. This material has been tested at IERL-RTP's pilot plant and at a full scale scrubber installation. The results show that the DBA material enhances the performance of the scrubbers similar to pure adipic acid. Since the DBA material is projected to cost only one-third to half the cost of adipic acid, this alternative is particularly attractive.

The testing to date has found that the adipic acid or DBA additive reduces energy requirements of the process over conventional limestone scrubbing processes. This results primarily from operating at a lower L/G and from reducing the solid waste handling requirements. The environmental impact of the enhanced process is about the same as conventional limestone scrubbing, except that the solid waste loading is less from the enhanced process. There is no significant difference in the toxicity of the wastes from the two processes.

Wet Lime/Limestone with Forced Oxidation(5)

A major advancement in the wet lime/limestone scrubbing process is the stabilization of the waste material by forced oxidation (e.g., air sparging into slurry hold tank). In the past, a disadvantage of lime/limestone scrubbing processes has been the large volume of waste solids produced. This waste slurry, consisting of predominantly calcium sulfite, could only be dewatered to about 50 to 60 percent solids, thus

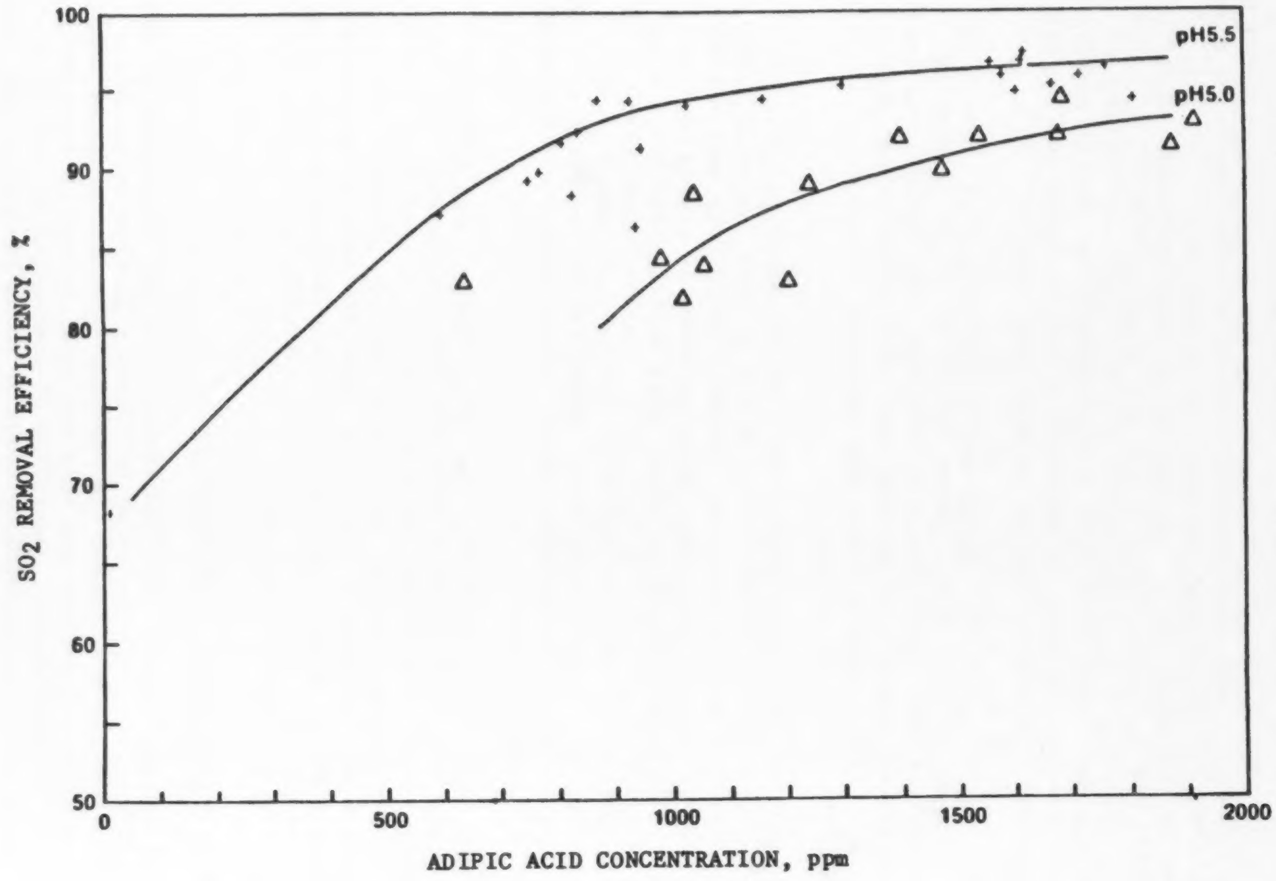

Figure 2. Effect of Adipic Acid Concentration and pH on SO_2 Removal Efficiency in Limestone Wet FGD(4)

producing a material which may be unsuitable for landfill. In the past, the primary utility practice involved the use of lined ponds for containment in order to prevent contamination of ground and surface waters. Although less expensive than other disposal options compatible with landfill, such as chemical fixation and fly ash blending, ponding of this material represented as much as 20 to 25 percent of the overall scrubbing process costs. Furthermore, the large land areas required for these disposal ponds were difficult to reclaim for other productive use due to the poor mechanical stability and load bearing strength of the waste material. One solution to the situation is the forced oxidation of the calcium sulfite produced to calcium sulfate (gypsum), a material easily dewatered to greater than 80 percent solids. Since, in the United States, by-product gypsum may be unable to compete with the widely available natural gypsum, the incentive has been to develop simplified low-cost forced-oxidation procedures directed primarily toward improving waste solids handling and disposal properties while minimizing waste disposal costs.

Wet ponding, landfilling, and mine disposal are three current means of disposal. Ponds can be designed based on diking or excavation and can even be engineered on slopes. A special case of wet ponding is FGD gypsum stacking. Gypsum slurry from the forced oxidation system is piped to a pond and allowed to settle, and the supernate recycled. Periodically the gypsum is dredged and stacked around the embankment. For disposal in a landfill, dewatered wastes are transmitted to the disposal site where they are spread on the ground to a thickness of about 0.3 to 1 meter. Compaction by heavy equipment follows, and a layering process proceeds at the site. A disposal method that is receiving increased attention is mine disposal, particularly in the West. Surface coal mines are the most likely candidates for FGD waste disposal. Coal mines offer the greatest capacity for disposal, and they frequently have direct transportation (e.g., rail) connections tied to power plants. In fact, many new coal-fired power plants are "mine-mouth" (located within a few kilometers of the mine), and the mine provides a dedicated coal supply. Since the amount of FGD wastes produced is considerably less than the amount of coal burned, such mines usually would have the capacity for disposal throughout the life of the power plant.

Surface mines have basically three options for the disposal of FGD wastes:

- In the working pit, following coal extraction, and prior to return of overburden.
- In the spoil banks, after return of overburden, but prior to reclamation.
- Mixed with, or "sandwiched" between, layers of overburden.

The latter two options appear to be more environmentally sound and are expected to show strong growth in the future.

Dual Alkali(6)

The dual alkali FGD process consists of four basic steps:

1. Flue gas pretreatment (optional).
2. SO_2 absorption.
3. Absorbent regeneration.
4. Solid/liquid separation and solids dewatering.

Figure 3 illustrates the process flow for a typical dual alkali FGD system.

During pretreatment, flue gas from the boiler can be routed through an electrostatic precipitator (ESP) to remove particles (fly ash) upstream of the absorber. Pretreatment can also involve wet scrubbing, alone or in series with the ESP, for particle and chloride removal. Pretreatment is not always necessary in dual alkali FGD; its use depends on site-specific conditions such as fuel characteristics and cost considerations.

The flue gas then flows to an absorber and is brought in contact with a recirculating solution containing an equilibrium mixture of sodium sulfite (Na_2SO_3), sodium bisulfite ($NaHSO_3$), sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), and sodium bicarbonate ($NaHCO_3$). SO_2 is absorbed by this solution and reacts with the alkali in solution to form soluble sulfur salts.

Desulfurized flue gas leaves the absorber, is reheated if necessary, and is exhausted through the stack to the atmosphere. A portion of the circulating absorbent solution is routed to the absorbent regeneration system to be reacted with lime, to precipitate the absorbed SO_x as:

- Calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2H_2O$).
- Gypsum ($CaSO_4 \cdot 2H_2O$) (only in dilute dual alkali systems).
- A mixed crystal of hydrated calcium sulfite/sulfate.

The precipitation reaction also regenerates soluble alkali for recycle to the absorber.

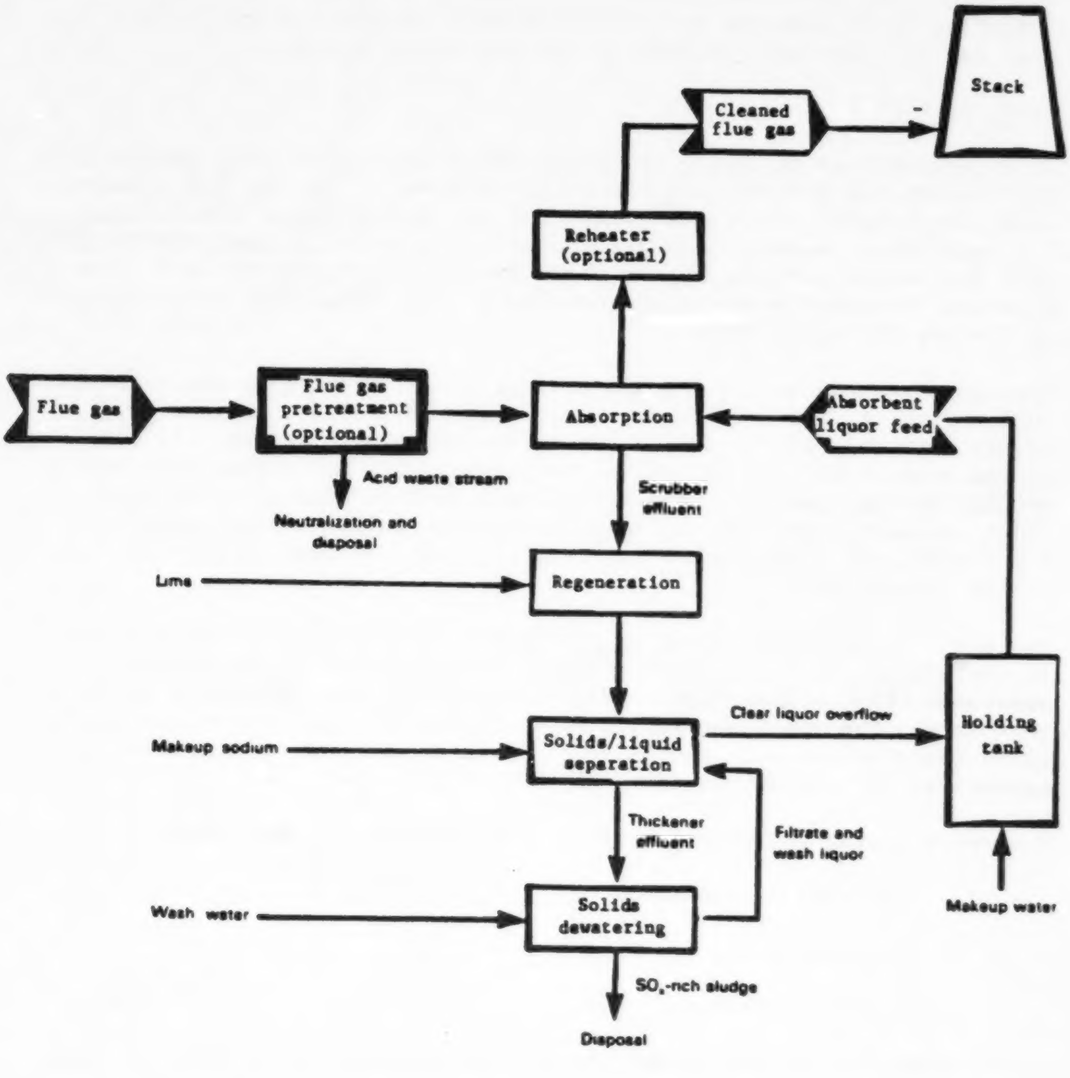
Stack
Cleaned flue gas
Reheater (optional)
Flue gas
Flue gas pretreatment (optional)
Absorption
Absorbent liquor feed
Acid waste stream
Neutralization and disposal
Scrubber effluent
Lime
Regeneration
Clear liquor overflow
Holding tank
Makeup sodium
Solids/liquid separation
Thickener effluent
Filtrate and wash liquor
Wash water
Solids dewatering
Makeup water
SO$_x$-rich sludge
Disposal

Figure 3. Dual Alkali FGD Process$^{(6)}$

The precipitated SO_x salts are separated from the scrubbing liquor and concentrated for disposal in the solid/liquid separation and solids dewatering steps. The solids settle out of the slurry in a clarifier-thickener; they are dewatered further in a vacuum filter or centrifuge and are washed to recover sodium salts before disposal. The clear liquor overflow from the clarifier-thickener is combined with makeup soda ash solution and returned to the absorption system.

Spray Drying(7)

Nonregenerable spray drying processes are presently the only commercially applied dry FGD processes in the United States. Other dry FGD processes under development include dry injection and combustion of coal/alkali-fuel mixtures. Several factors, including increases in coal use and the 1979 new source performance standards (NSPS) for utility boilers, have promoted increased research and development and commercial application of the dry FGD technology.

Interest in spray drying FGD has primarily been spurred by the potential cost savings dry FGD offers over conventional wet FGD, particularly for low-sulfur coal (less than 1.5 percent sulfur) applications. In addition to the production of a dry waste, advantages of spray drying FGD over wet FGD systems include potentially lower initial capital investment, lower operating costs for up to moderate fuel sulfur content (possibly 3 percent), and less process complexity, which may lead to greater system reliability.

The major disadvantage of spray drying FGD relative to wet FGD systems is the higher absorbent cost, which results from the higher priced absorbent (lime versus limestone) and the higher stoichiometric ratios necessary. The applicability of spray drying FGD for high-sulfur coal-fired installations is limited by the lack of data on the SO_2 removal capability and the higher costs of this technology.

The spray drying FGD process (Figure 4) consists of three steps:

1. Absorbent preparation.

2. SO_2 absorption drying.

3. Solids collection.

For economic comparison of wet and dry FGD systems, waste disposal cost should also be included. In this regard, waste disposal would be the last step of each of the process steps for FGD systems.

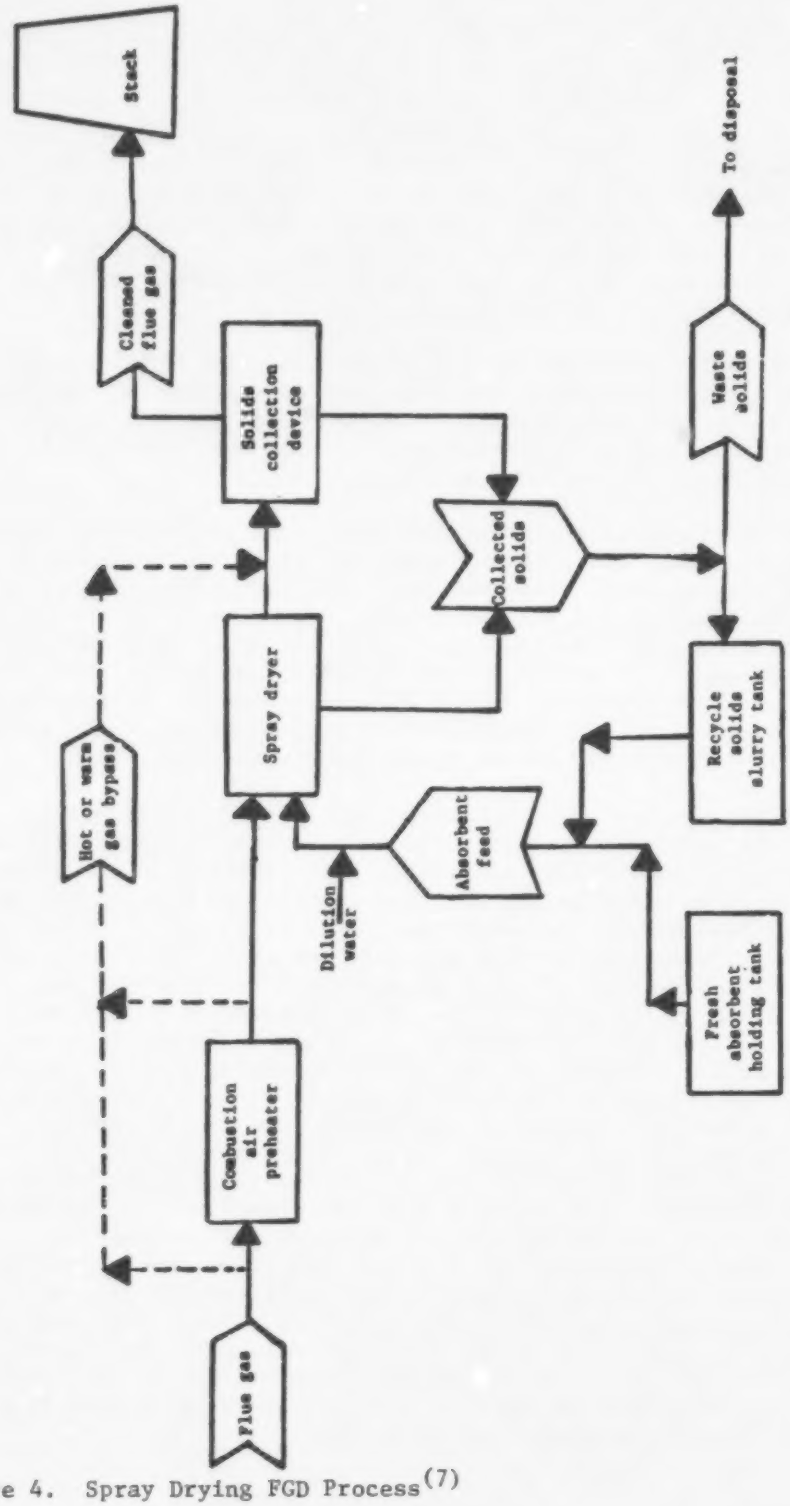
Flue gas
Combustion air preheater
Hot or warm gas bypass
Spray dryer
Solids collection device
Cleaned flue gas
Stack
Collected solids
Waste solids
To disposal
Recycle solids slurry tank
Absorbent feed
Dilution water
Fresh absorbent holding tank

Figure 4. Spray Drying FGD Process(7)

Flue gas exiting the combustion air preheater is contacted with an alkaline solution or slurry in a spray dryer. In the spray dryer, the flue gas passes through a contacting chamber, and the solution or slurry is sprayed into the chamber with a rotary or nozzle atomizer. The heat of the flue gas dries the atomized droplets, while the droplets absorb SO_2 from the flue gas. The SO_2 reacts with the alkaline reagent to form solid-phase sulfite and sulfate salts.

Most of these solids (and any fly ash present) are carried from the dryer in the exiting flue gas. The rest fall to a hopper at the bottom of the dryer. In contrast to wet FGD systems, the flue gas is not saturated with moisture after the absorption step but is within 11 to 28°C (20 to 50°F) of the saturation temperature(8).

The solution or slurry is pumped to the dryer from an absorbent holding tank. Fresh absorbent and dilution water are added to this tank as needed. (In some systems, dilution water for temperature control in the spray dryer is added to the absorbent feed just upstream of the spray dryer.) Recycle solids from the spray dryer hopper or downstream solids collection equipment contain unreacted absorbent and may be used to supplement the fresh absorbent feed. Recycle solids are either slurried separately and added to the absorbent feed just upstream of the spray dryer or are added directly to the fresh absorbent holding tank.

Flue gas may be reheated after it leaves the spray dryer to prevent condensation in downstream solids collection equipment. Reheating may be desirable and economically justifiable: SO_2 removal in the spray dryer is greatly improved as the flue gas temperature approaches the saturation temperature of the gas at the spray dryer exit. Reheat may be accomplished by mixing the flue gas from the spray dryer with either hot flue gas from upstream of the combustion air preheater or warm flue gas from upstream of the spray dryer. Other methods of reheat could be used such as heating air and injecting it into the cleaned flue gas, heating part of the cleaned flue gas and re-injecting it into the remainder of the gas stream, or heating all the treated flue gas in a surface heat exchanger upstream of the particle collection device. Also note that using dirty flue gas (either warm or hot) for reheating means that higher SO_2 removal is required of the spray dryer to meet given emission limits. The reheated flue gas then flows to the solids collection device where the dry solids (which consist of reaction products, unreacted absorbent, and fly ash) are collected. A fabric filter (baghouse) is the most common solids collection device, but electrostatic precipitators (ESPs) are also used. When a baghouse is used, significant absorption of SO_2 may occur during the solids collection step. Absorbent in the solids collected on the surface of the bags reacts with SO_2 remaining in the flue gas, and the desulfurized flue gas is exhausted to the atmosphere through a stack.

While sodium compounds may serve as absorbents, most nonregenerable spray dryer FGD applications use lime because of its lower cost and the more stable wastes produced through its use(9). Since dry waste solids are generated in dry FGD processes, their disposal is typically by landfill. With sodium compounds (e.g., soda ash) as absorbents, the high water solubility of the resulting sodium salt wastes could require expensive lined landfills to control leaching into the ground water.

REGENERABLE FGD SYSTEMS

There are two primary regenerable wet FGD systems currently available for commercial applications: Magnesium Oxide and Wellman-Lord. Two other processes, the aqueous carbonate and citrate processes, are under development. These systems are capable of removing 90 to 95 percent of the flue gas SO_2(10).

The principal advantages of regenerable FGD systems over nonregenerable systems are the economic advantages gained from the reduction of waste disposal problems and the sale of recovered by-products. Wastewater streams are collected and can be neutralized by standard treatment systems, and most of the spent solution can be recirculated to the process. Solid waste loads are also considerably reduced. On the other hand, regenerable systems are more complex than current nonregenerable systems and generally involve higher capital investment and higher operating costs.

Wellman-Lord(11)

The Wellman-Lord process consists of four basic steps:

1. Flue gas pretreatment.
2. SO_2 absorption.
3. Purge treatment.
4. Sodium sulfite regeneration.

A fifth step, the processing of SO_2 into by-product sulfur, is not a part of the Wellman-Lord process but is generally associated with Wellman-Lord installations. Figure 5 illustrates the process flow for a typical Wellman-Lord system installed on a coal- or oil-fired boiler.

Boiler flue gas is pretreated by contact with water, usually in a venturi scrubber. This step cools and saturates the gas, absorbs corrosive chlorides, and removes some of the particles remaining in the gas after upstream particle removal efforts.

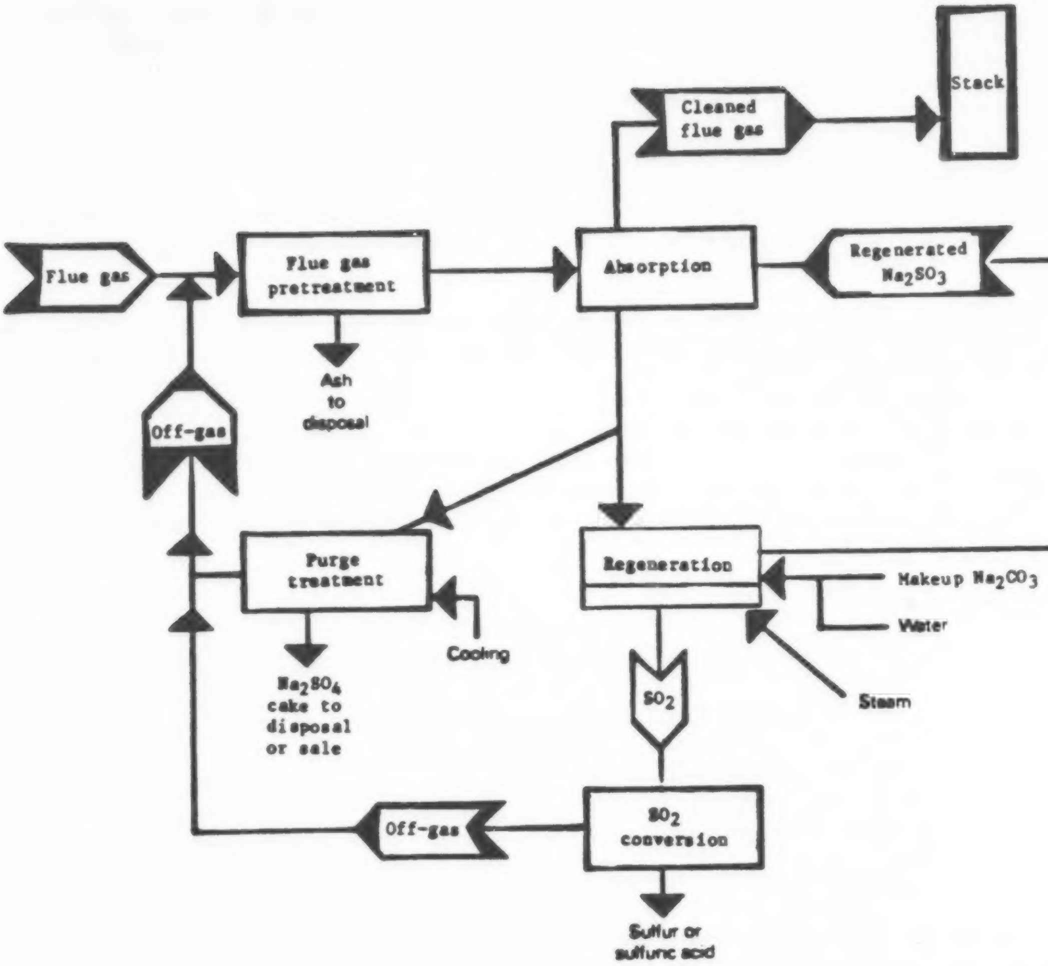
Stack
Cleaned flue gas
Flue gas
Flue gas pretreatment
Absorption
Regenerated Na_2SO_3
Ash to disposal
Off-gas
Purge treatment
Regeneration
Makeup Na_2CO_3
Water
Cooling
Steam
Na_2SO_4 cake to disposal or sale
SO_2
Off-gas
SO_2 conversion
Sulfur or sulfuric acid

Figure 5. Typical Wellman-Lord Process(11)

The flue gas then flows to an absorber where it is contacted with a sodium sulfite (Na_2SO_3) solution. The SO_2 in the flue gas reacts with the Na_2SO_3 to produce sodium bisulfite ($NaHSO_3$). In a side reaction, some sodium sulfate (Na_2SO_4) is formed by direct oxidation of Na_2SO_3.

Desulfurized flue gas leaves the absorber, is reheated to improve plume buoyancy and to vaporize any liquid droplets present, if necessary, and is exhausted through the stack to the atmosphere. If reheat is not used, then protective linings in stacks and acid-corrosion-resistant material in ducts are generally used in wet FGD applications. The effluent from the absorption tower, rich in $NaHSO_3$ and also containing some Na_2SO_3 and Na_2SO_4, is split into two streams. Approximately 15 percent of the effluent is routed to a purge treatment for sulfate removal. The remaining 85 percent goes to a regeneration process.

The purge stream is cooled in a chiller and a mixture of Na_2SO_4 and Na_2SO_3 is crystallized out of the solution. This crystalline mixture is removed from the process and dried for sale or disposal.

Regeneration is accomplished in an evaporator where the remainder of the SO_x absorber effluent is heated to convert $NaHSO_3$ to Na_2SO_3 and to drive off SO_2. The regenerated Na_2SO_3 crystallizes and then is redissolved and recycled to the absorber. Sodium lost during the process, primarily from the purge operation, is replenished by adding sodium carbonate (Na_2CO_3) to the feed dissolving tank.

The fifth step, SO_2 processing, uses the SO_2 by-product from the Wellman-Lord process. The output of the Wellman-Lord process is a gas stream of about 85 percent SO_2; the remainder is mostly water vapor. This concentrated SO_2 stream may be dried and marketed without further processing, reduced to elemental sulfur, or oxidized and reacted with water to form sulfuric acid (H_2SO_4).

Magnesium Oxide(12)

The magnesium oxide (MgO or Mag-Ox) FGD process consists of four major processing steps:

1. Flue gas pretreatment.
2. SO_2 absorption.
3. Solids separation and drying.
4. Regeneration.

SO_2 processing may be considered a fifth step because it is often associated with the MgO FGD process. Figure 6 illustrates the process flow for a typical MgO FGD system.

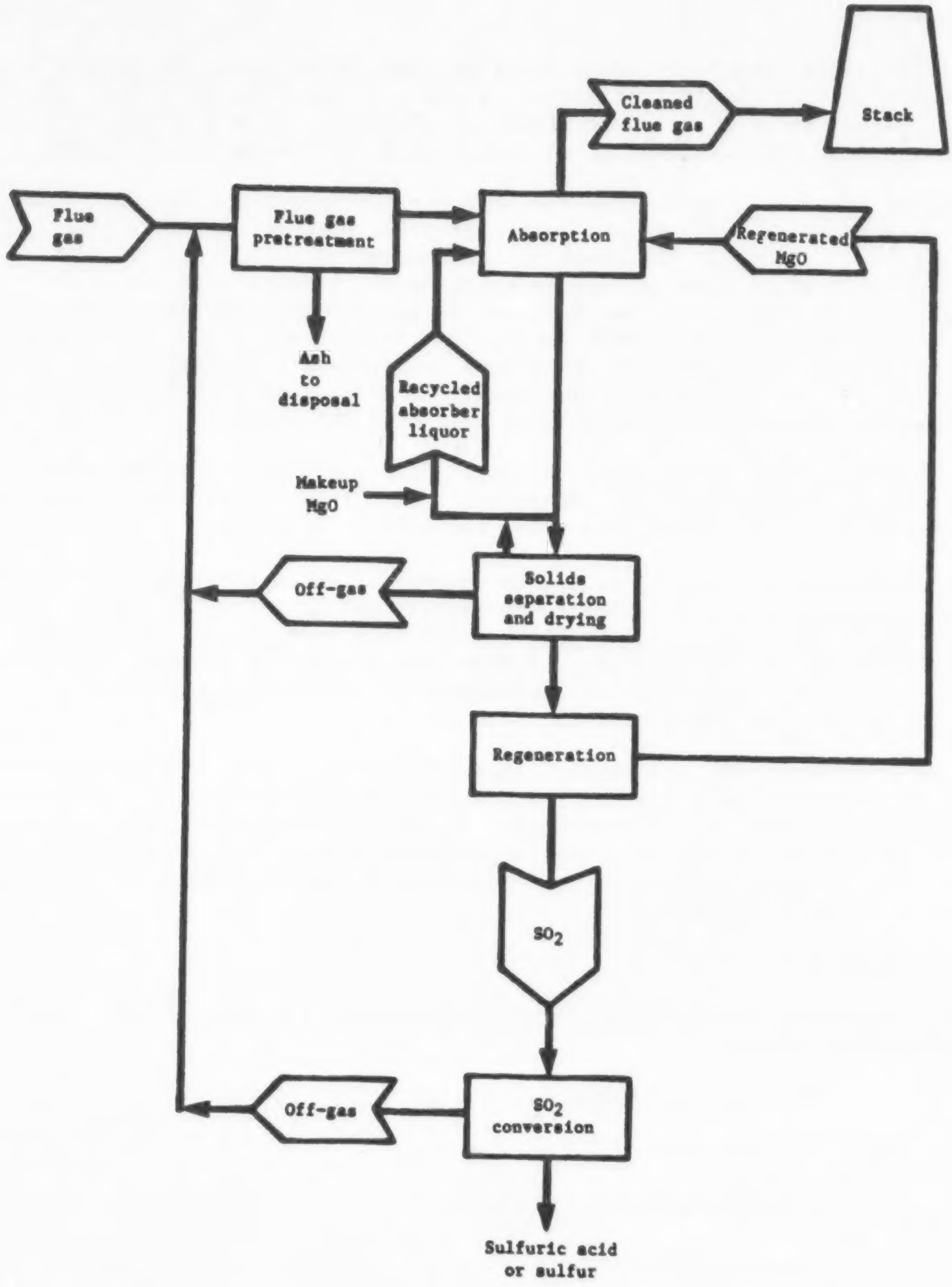
Cleaned flue gas
Stack
Flue gas
Flue gas pretreatment
Absorption
Regenerated MgO
Ash to disposal
Recycled absorber liquor
Makeup MgO
Off-gas
Solids separation and drying
Regeneration
SO_2
Off-gas
SO_2 conversion
Sulfuric acid or sulfur

Figure 6. Magnesium Oxide FGD Process with Regeneration and SO_2 Conversion(12)

In the first step, water scrubbing cools and saturates the boiler flue gas and removes fly ash and chlorides upstream of the absorber. While flue gas from oil-fired boilers generally does not require pretreatment by quenching, this step is necessary in coal-fired applications.

In the absorber (Step 2), SO_2 is removed from the flue gas by contact with a recirculating slurry of magnesium oxide (MgO), magnesium sulfite ($MgSO_3$), and magnesium sulfate ($MgSO_4$). Flue gas SO_2 is absorbed by this slurry and reacts with MgO to form $MgSO_3$, some of which reacts with oxygen (O_2) present in the flue gas to form $MgSO_4$. Additional $MgSO_4$ is formed when flue gas sulfur trioxide (SO_3) reacts with MgO.

Desulfurized flue gas leaves the absorber, is reheated if necessary, and is exhausted through the stack. The scrubbing liquor is continuously recycled to the absorber after a continuous bleed stream has been withdrawn from the recirculation loop for solids separation and regeneration processing. Fresh MgO slurry is added to the recirculation loop to replace the scrubbing liquor removed by the bleed stream.

In the third step, the bleed stream is routed to a centrifuge where it is concentrated to 60 percent solids by weight, and the mother liquor is recycled to the absorber recirculation loop. The concentrated solids flow to a dryer where surface moisture and most of the water of hydration are removed, producing a dry powder of $MgSO_3$, $MgSO_4$, unreacted MgO, and inert materials.

Calcination of the dry powder in the regeneration processing stage (Step 4) converts $MgSO_3$ and $MgSO_4$ to MgO, which is recycled to the absorber recirculation loop. $MgSO_4$ is reduced with coke during the calcination process. Calcination also produces an SO_2-rich by-product stream that may be processed further to form sulfuric acid or elemental sulfur.

Thus, the MgO FGD process not only regenerates the essential absorbent, MgO, but also produces SO_2 at concentrations practical for conversion to sulfuric acid or elemental sulfur.

Aqueous Carbonate(13)

The aqueous carbonate process can be divided into four major operations: flue gas handling, SO_2 absorption and product collection, absorbent regeneration, and sulfur production. Figure 7 is a process flow diagram of a typical aqueous carbonate system.

Flue gas is contacted with sodium carbonate solution in a spray dryer, and SO_2 is absorbed. The solid sodium sulfite and sodium sulfate formed is collected in cyclones and an ESP. The flue gas, which is only partially quenched, is emitted to the atmosphere without reheating. Overall reactions in the spray dryer are:

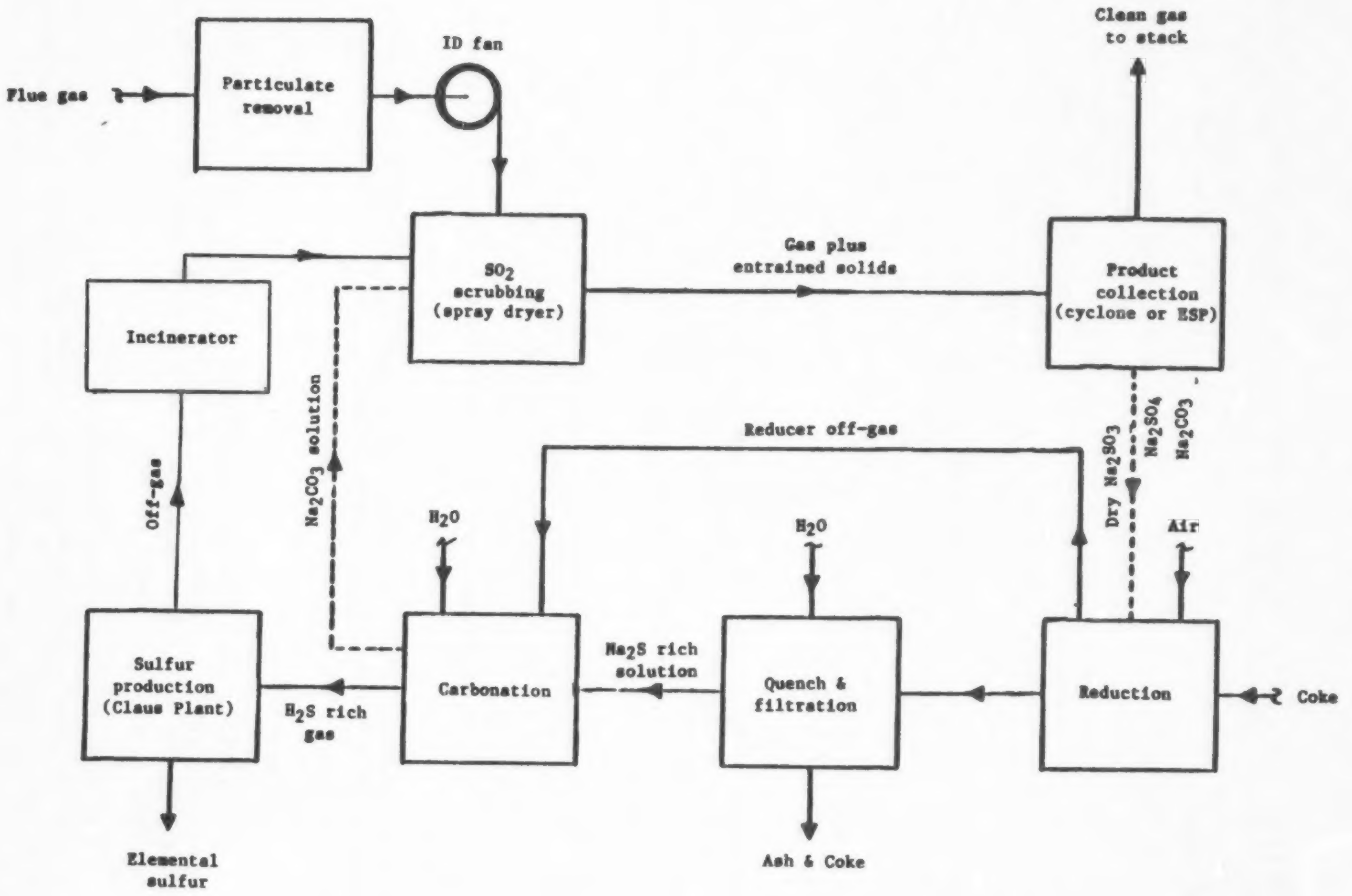
Flue gas
Particulate removal
ID fan
Clean gas to stack
SO_2 scrubbing (spray dryer)
Gas plus entrained solids
Product collection (cyclone or ESP)
Incinerator
Na_2CO_3 solution
Reducer off-gas
Dry Na_2SO_3
Na_2SO_4
Na_2CO_3
Off-gas
H_2O
H_2O
Air
Sulfur production (Claus Plant)
H_2S rich gas
Carbonation
Na_2S rich solution
Quench & filtration
Reduction
Coke
Elemental sulfur
Ash & Coke

Figure 7. Aqueous Carbonate FGD Process(13)

$SO_2 + Na_2CO_3 \rightarrow Na_2SO_3 + CO_2 \uparrow$ (1)

$Na_2SO_3 + 1/2\ O_2 \rightarrow Na_2SO_4$ (2)

In the regeneration area, spent absorbent is melted, mixed with coal or petroleum coke, and sparged with air in the reducer vessel. The following reactions occur:

$Na_2SO_3 + 2\ C + 1/2\ O_2 \rightarrow Na_2S + 2\ CO_2$ (3)

$Na_2SO_4 + 3\ C + O_2 \rightarrow Na_2S + 3\ CO_2$ (4)

A portion of the smelt is continuously withdrawn to a quench tank and dissolved in water. The "green liquor" thus produced is clarified, filtered, and contacted with the cooled reducer off-gas in a series of tray towers to regenerate sodium carbonate and evolve hydrogen sulfide by the following reactions:

$Na_2S + 2\ CO_2 + 2\ H_2O \rightarrow H_2S + 2\ NaHCO_3$ (5)

$2\ NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$ (6)

The regenerated liquor is filtered and recycled to the spray dryer/absorber. Solids, mainly composed of ash and miscellaneous impurities, from the green liquor filters and from the regenerated liquor filters are disposed of.

Sulfur production involves the conversion of H_2S to elemental sulfur in a three-stage Claus unit. The tail gas from the unit is incinerated and recycled to the spray dryer/absorber.

Currently no dry FGD systems use regeneration, although those using Na_2CO_3 in spray dryers duplicate the absorption step of the aqueous carbonate process.

ECONOMIC COMPARISONS

Cost estimates for most wet FGD processes are readily obtained from the wealth of design and operating experience for these processes. Cost projections for the only dry FGD (spray dryer) process yet commercialized are based on pilot- and demonstration-scale tests and vendor estimates. As TVA has performed comprehensive studies for EPA on the economics of FGD, costs from these studies are the bases for the comparisons reported here.

The state-of-the-art wet FGD system is considered to be the nonregenerable limestone spray tower process. Other wet FGD systems are compared with this system, the costs for each system having been determined using the same design and economic premises(14,15,16). Since the costs of the processes ranked in Table 1 are being updated to conform to the 1979 NSPS for utility boilers and revised design and economic premises, no numerical values are listed. Table 1 ranks these processes in order from lowest to highest costs.

A comparison of dry FGD (spray dryer) costs with wet limestone FGD (spray tower) costs is given in Table 2(9). The costs include particulate matter removal and waste disposal because particulate matter removal is an inherent part of the dry FGD process. While wet FGD costs are founded on extensive design and operating experience, only limited pilot- and demonstration-scale data are available for dry FGD. Since the same estimation basis and methods were used for each process evaluated, the accuracy for comparison is reasonable for preliminary studies.

Table 2 shows that the capital investment and first year revenue requirements for dry FGD are less than those for wet FGD for all cases compared. For high sulfur coal (3.5 percent sulfur), however, the lifetime cost for wet limestone FGD is about 2 percent less than for lime spray drying. While the capital investment advantage for the lime spray dryer over the wet limestone process ranges from about 14 to 30 percent, the annual revenue requirement advantage for the spray dryer over the wet limestone process falls from about 28 to 2 percent for increasing sulfur content of the eastern coals. This is attributed to the higher unit cost and the higher stoichiometric ratio for the lime system relative to the limestone system. By increasing the sulfur content of the coal from 0.7 to 3.5 percent, the absorbent costs increase about 10-fold and represent about 27 percent of the first year revenue requirements for the lime spray dryer, while corresponding values for the wet limestone FGD system are 7-fold and 3 percent.

Table 2 also indicates that the lime spray dryer would be the economic choice over soda ash spray drying for low-sulfur western coal. Because of the higher unit cost of soda ash relative to lime, the expected sources for soda ash being in the West, and high disposal costs for sodium salt wastes, the economic advantage of the lime over the soda ash spray dryer is expected to be even greater at eastern sites.

As noted earlier, the addition of adipic acid to the wet limestone FGD process improves both SO_2 removal and limestone utilization. Both of these improvements lead to decreased lifetime cost, and the quantification of their effects is underway. Limited pilot plant testing also showed adipic acid to improve both SO_2 removal and sorbent utilization when either lime or limestone are used in spray drying with partial recycling of waste solids(17). However, the low reactivity of limestone at the usual flue gas conditions in spray drying apparently limits SO_2 removal

TABLE 1. COMPARATIVE ECONOMICS OF ALTERNATE WET FGD PROCESSES IN ORDER OF INCREASING COSTS(14,15,16)

Lifetime Cost	Capital Investment	First Year Annual Revenue Requirements	Waste or By-product
Limestone	Lime	Limestone	Waste
Dual alkali	Limestone	Dual alkali	Waste
Lime	Dual alkali	Lime	Waste
Aqueous carbonate	Aqueous carbonate	Aqueous carbonate	By-product
Magnesium oxide	Wellman-Lord/acid	Magnesium oxide	By-product
Wellman-Lord/acid	Magnesium oxide	Wellman-Lord/acid	By-product
Wellman-Lord/RESOX	Wellman-Lord/RESOX	Wellman-Lord/RESOX	By-product
Citrate	Citrate	Citrate	By-product

NOTES:

1. Credit is taken for the sale of by-products for the last five processes listed.
2. Particulate matter removal and waste disposal costs are not included for any process listed.
3. Design and economic premises are: new 500-MWe midwestern plant firing eastern bituminous coal (3.5% S, 12% ash, 5833 kcal/kg (10,500 Btu/lb), 30-year plant life, and SO_2 emissions meeting 1971 NSPS).

TABLE 2. COMPARATIVE ECONOMICS FOR DRY (SPRAY DRYER) AND WET LIMESTONE FGD PROCESS FOR SEVERAL COALS AND SULFUR CONTENTS(7,9)

Process	Fuel	Lifetime Cost, $\$10^6$	Capital Investment $\$10^6$	First Year Annual Revenue Requirements, $\$10^6$
Lime spray dryer	Lignite	860.8	82.6	20.9
Limestone wet FGD	0.9% S	1069.5	107.4	26.3
Soda ash spray dryer	Subbituminous (western) coal	844.4	79.4	20.4
Lime spray dryer	0.7% S	774.7	77.1	19.0
Limestone wet FGD		885.5	88.1	21.7
Lime spray dryer	Bituminous	757.1	75.3	18.6
Limestone wet FGD	(eastern) coal 0.7% S	936.4	92.6	23.9
Lime spray dryer	Bituminous	1413.3	100.1	31.9
Limestone wet FGD	(eastern) coal 3.5% S	1355.8	121.9	32.4

BASIS: A new 500 MWe plant is assumed to be located in Wyoming, Colorado, Nebraska, North Dakota, or South Dakota when lignite or low sulfur western coal is the fuel. A midwestern plant site (Kentucky, Illinois, or Indiana) is used for the eastern coal estimates. TVA design and economic premises were applied with capital investment expressed in 1982 dollars. Investment costs include those for control of SO_2 emissions and disposal of scrubber waste via landfilling 1.6 km (1 mi) from the plant site. The plant has an operating life of 165,000 hours over a 30-year period (equivalent to full load over 5500 hr/yr). The boiler heat rate is 2394 kcal/kWh (9500 Btu/kWh) for coal and 2948 kcal/kWh (11700 Btu/kWh) for lignite. Revenue requirements are in 1984 dollars, while the total evaluated cost is based on a fixed charge rate of 14.7 percent and a levelized operation and maintenance factor of 1.886, which account for inflation and the cost of money over the plant life.

FUEL DATA:

	As Fired				Dry Basis
	Heating Value kcal/kg	Heating Value Btu/lb	Ash %	Moisture %	Sulfur %
Lignite	3667	6600	7.2	36.3	0.9
Western Coal	5390	9700	9.7	16.0	0.7
Eastern Coal	6501	11700	15.1	4.0	0.7
Eastern Coal	6501	11700	15.1	4.0	3.5

to about 30 to 35 percent. While the apparent improved performance using adipic acid in the wet FGD system may exceed that in the spray dryer, the impact this additive has on lifetime cost may be greater for the dry FGD system because of the relative effect of sorbent cost on revenue requirements (as noted earlier). Consequently, further work is needed to definitize the cost effect of adipic acid additive on both of these FGD processes.

SUMMARY

Wet FGD processes can effectively and reliably control SO_2 emissions from coal-fired boilers. Among the available wet processes, the nonregenerable (throwaway) wet limestone system predominates the power plant applications because of its cost advantage. A recent improvement to the wet limestone/lime FGD process is the use of forced oxidation to produce a more suitable waste product (gypsum) for landfill disposal. Currently, the addition of adipic acid to limestone is demonstrating improved SO_2 removal (consistently above 90 percent) and sorbent utilization (over 95 percent) and appears to offer significant performance improvement and cost savings.

Dry FGD has recently emerged as a potentially more economical and reliable option for low-to-moderate-sulfur coal applications. Its viability remains to be demonstrated in full-scale applications: the first utility system is slated for operation this year. The lime-based spray dryer appears to offer capital investment savings due to its simpler design, but it requires lime which is more expensive than limestone. The application of dry FGD to high-sulfur coal may be enhanced by using adipic acid in the lime spray dryer method.

Regenerable FGD processes offer sulfur or sulfuric acid as by-products. The Wellman-Lord process is being used at several power plants and a 100-MWe demonstration of the aqueous carbonate process is in the construction phase. Generally, the higher lifetime costs and the markets for these by-products have not encouraged widespread selection of regenerable FGD processes.

Wastes from nonregenerable FGD processes are classed as nonhazardous, with disposal by landfill becoming the general practice. Forced oxidation has improved the disposal characteristics of wastes from the wet limestone FGD process, making these wastes more suited to landfill disposal. Dry wastes from lime spray dryers are well-suited to landfill disposal, but the use of sodium compounds in dry FGD may require lined landfills to limit the leaching of sodium salts into ground water.

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HEALTH AND ENVIRONMENTAL STUDIES OF COAL GASIFICATION PROCESS STREAMS AND EFFLUENTS

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ABSTRACT

The Synfuels Environmental Research Program at Argonne National Laboratory is investigating the impact of high-BTU coal gasification on health and the environment. Activities include a toxicologic and chemical characterization of process streams in the gasifier and pretreater sections of the HYGAS coal gasification pilot plant, and process streams and workplace air from the Grand Forks Energy Technology Center's slagging fixed-bed gasifier facility. Cellular assays for mutagenicity, cytotoxicity, and functional impairment are performed to determine relative toxicity. Various acute and chronic whole animal toxicological evaluations, including skin tumorigenesis, are performed for streams found to contain potential toxicants (e.g. oils and tars). The chemical characteristics of vapor phase and airborne particulate-associated organics, as well as biologically active materials isolated from process streams, are investigated by physical and chemical fractionation of the samples, with biological monitoring and detailed GC and GC/MS analyses of the fractions. Present data indicate that toxicants are present, but their levels of activity are relatively low. As a result of these studies, we tentatively conclude that with appropriate control technology and industrial hygiene procedures there appear to be no serious health or environmental problems associated with coal gasification.

INTRODUCTION

A thorough evaluation of the potential impact on human health and the environment is a prerequisite to implementation of new fossil fuel conversion technologies. The Department of Energy (DOE), through its Offices of Energy Research and Fossil Energy, sponsors several research programs to provide this evaluation. Argonne National Laboratory has the major responsibility in the area of high-BTU coal gasification, and thus has the obligation to develop:

- A comprehensive health and environmental data base for coal gasification

- A reliable assessment of the risks associated with large-scale coal gasification

Projects within Argonne's Synfuels Environmental Research Program include a completed study of the HYGAS pilot plant at the Institute of Gas Technology (IGT) Energy Development Center (Chicago, IL) and ongoing studies of the slagging fixed-bed gasifier at the Grand Forks Energy Technology Center (GFETC) (Grand Forks, ND), and a bench scale gasifier at the Carnegie-Mellon Institute of Research (Pittsburgh, PA). This report discusses the HYGAS pilot plant studies and gives initial results from GFETC. Experiments with the Carnegie-Mellon gasifier samples were only recently initiated and will not be presented.

The Argonne program employs an integrated multidisciplinary approach to sample characterization. Sample preparation and fractionation activities, toxicological characterization, and identification of specific chemical components required interaction and collaboration among personnel in three Argonne Divisions:

Analytical Chemistry Laboratory (Chemical Engineering Division)
Biological and Medical Research Division
Energy and Environmental Systems Division

BACKGROUND

The end product of high-BTU coal gasification is a substitute natural gas (SNG), essentially indistinguishable from natural gas, and therefore presents no new health or environmental issues. However, most gasification processes also produce by-product oils and tars known to contain a variety of noxious chemicals, including carcinogens. These oils and tars are extremely complex mixtures and are at present chemically illdefined. Although these potentially toxic by-products are readily removed from the product gas and can be completely consumed on site, potential routes of human exposure do remain - namely, direct contact with solids and liquids, or inhalation of fugitive vapor, aerosol and particulate emissions. This program emphasizes the toxicological and chemical characterization of the organic components of process streams. This report summarizes our activities to date at IGT and GFETC. Additional more detailed information has appeared elsewhere (1-5).

PROCESS DESCRIPTIONS

HYGAS

This advanced process for high-BTU coal gasification was developed by IGT with support from the Gas Research Institute and DOE. An 80 ton per day pilot-plant gasifier has operated for several years on a variety of coal types. A detailed description of the process, the operating conditions during sampling, and the samples that were collected is included in a recent report presented at the Second International Gas Research Conference (6).

Emphasis in this report is placed on the pilot plant process streams deemed to be of environmental importance in commercial facilities. Samples from the low temperature reactor (LTR) provide a reasonable approximation of the organic compounds formed during coal gasification. Not all of these organic compounds leave the gasifier, but those that do enter the recycle oil. The recycle oil system, which accounts for the largest mass flow of organics within a plant, has the greatest potential for leaks and fugitive emissions. It is also the most significant environmentally, since it will represent a steady-state composition of high molecular weight organic compounds leaving the gasifier. Organics formed in the coal pretreatment process also could be a major source of fugitive emission in the commercial plant. In the pilot plant these organic compounds are found in the pretreater quench water. Finally, organic compounds present in the gasifier quench water, if not removed in the water treatment system, could enter the atmosphere through cooling tower water desorption. Although spent char is a significant plant discharge stream, it would be incinerated in a commercial plant and thus is not considered to be environmentally important.

SLAGGING FIXED-BED GASIFIER

The gasifier operated by GFETC is a 25 ton per day slagging fixed-bed pressurized gasifier which differs from other fixed-bed gasifiers in that a lower steam:oxygen ratio is used for the gasification reaction, and operating temperatures are high enough to melt the ash for discharge as a molten slag. This gives the slagging process several advantages, including higher throughput, lower steam consumption, and lower wastewater production. A detailed description of the process was presented at the 1981 Lignite Symposium (7).

Waste effluent streams from a fixed-bed gasification process consist of (a) gaseous contaminants (chiefly H_2S, CO_2, and light hydrocarbons), which are cleaned from the product gas by commercially available processes to meet end use requirements; and (b) solid and liquid effluent streams consisting of slag, slag quench water, and the gas liquor, composed of condensed tar, oil, water, and coal dust entrained in the product gas. Additional solid wastes may also be generated by wastewater treatment processes. Emphasis in our studies has been placed on what is considered to be potentially the most noxious gasifier waste stream, the gas liquor obtained from the condensation of tars, oils, and water in the spray cooler. While the GFETC gasifier is slightly different from a commercial design, the chemical nature of the tar and oil should be more dependent on the nature of the feed coal than of gasifier design.

METHODOLOGY

SAMPLING

All process stream samples were collected by the plant operators under conditions of steady operation. Following collection, the samples were refrigerated (4°C) and shipped to Argonne. At Argonne a locked refrigerated storage vault was used. Detailed records were systematically maintained to document sample preparation, transfer to and from storage, fractionation, and subsequent distribution.

The HYGAS samples studied were from the final four HYGAS test runs, all of which used a Western Kentucky feed coal. Samples from GFETC came from a test run that used North Dakota Indian Head lignite. Samples were collected from the tar-oil separator and consisted of process oil, tar, and water.

Samples of airborne particulates and fugitive organic vapors were collected by Argonne personnel in collaboration with GFETC process and environmental engineers at various locations in the gasifier building. Vapor samples were collected on XAD-2 resin at level 2 (steam injection and control room) and level 7 (lockhopper) during a run with Indian Head lignite. The resin was extracted with methylene chloride and the organic compounds present in the extract were identified by GC/MS and quantified by GC. Procedures and techniques have been reported in an earlier study concerning sampling at the HYGAS facility (5).

Particulate sampling was conducted during shutdown operations and operation of the gasifier following an aborted start up. A size-fractionated particle sample collected with a Sierra high-volume impactor was subjected to analysis by GC/MS and scanning electron microscopy; aerosols collected with an Anderson low-volume impactor were subjected to flameless atomic absorption analysis.

TOXICOLOGY

Three cellular tests were used to establish relative toxicities of all process samples. This battery of procedures was required to provide the variety of toxicological end points and systems necessary to evaluate the broad chemical spectrum of compounds present in the sample materials. The Ames *Salmonella* plate incorporation assay was used to determine mutagenicity. Strain TA98 was used exclusively because it was found to be the most sensitive of the five commonly used strains. Metabolic activation of samples with rat liver S9 enzymes was essential for expression of mutagenicity. Mouse myeloma cells were used to measure both genotoxicity (by sister chromatid exchange) and cytotoxicity (by growth inhibition). Finally, two additional measures of cytotoxicity, a gross measure (cell death) and a subtle measure (loss of normal cell function), were obtained using the rabbit alveolar macrophage (RAM) assay. The functional loss was evaluated by determining the inhibition of normal phagocytic activity in these cells.

In addition, whole animal toxicological assays were performed on HYGAS recycle oil. The assays included measurement of the effects of both acute and chronic dermal exposures and acute ocular exposures. Dermal effects were studied in SKH hairless mice (carcinogenicity), albino guinea pigs (hypersensitivity), and New Zealand albino rabbits (acute effects).

Ocular tests were performed in New Zealand albino rabbits.

BIO-DIRECTED CHEMICAL CHARACTERIZATION

Chemical characterization of samples was always performed in support of toxicological determinations. Table 1 gives the procedures employed. Many of the process samples were heterogeneous and not suited for direct testing in the cellular assay systems. Materials were physically separated and the organic components were extracted from the aqueous and solid phases. The resulting extracts and oils were then fractionated on the basis of volatility. In our experience only the nonvolatile organic (NVO) fractions containing components boiling at greater than $\gtrsim$ 200°C exhibited mutagenic activity and thus were the materials entered in the toxicity screening tests. Materials found to show significant toxicity in the test screen were further fractionated on the basis of acidity and polarity. Mutagenic activity in the various fractions was monitored with the Ames *Salmonella* assay. Chemical fractionation procedures included both liquid/liquid partitioning and high efficiency column chromatography. GC/MS was used for identification of the components in a given fraction and fused silica capillary column GC was used for quantification (1).

TABLE 1. BIO-DIRECTED CHEMICAL CHARACTERIZATION

- Physical Fractionation
  - Phase
  - Volatility

- Chemical Fractionation
  - Acidity
  - Polarity

- Biomonitoring (Ames assay)
- Chemical Testing (Nitrous acid)
- Compound Identification (GC/MS)
- Compound Quantification (GC)

RESULTS

Information is available for scores of samples and fractions of HYGAS materials and is rapidly accumulating for the GFETC gasifier. Presentation of HYGAS results is restricted to average toxicities observed in process streams deemed to be significant, either by the degree of toxicity or the potential for human exposure. GFETC data, being preliminary in nature, is restricted to process tars and oils, which are the putative major toxicants.

The streams that are discussed, and their approximate mass flow rates relative to feed coal are shown in Table 2.

TABLE 2. SIGNIFICANT PILOT PLANT STREAMS

Stream	Mass Flow (coal = 1)
HYGAS	
Recycle Oil	3
Pretreater Quench Water	3
Gasifier Quench Water	1
Low Temperature Reactor Gas	1.4
GFETC Gasifier	
Tars and Oils	0.05
Water	0.6

It is important to emphasize that the mutagenicities of HYGAS process samples were too low to measure directly and the toxicity data presented applies only to the NVO fraction. These fractions always constitute a very small part of the process stream (0.1 to 4 weight percent of the sample). Process stream toxicities (calculated as the product of NVO toxicity and its weight fraction) are accordingly quite low. Tars and oils from the GFETC gasifier have relatively greater weight percent of NVO's: approximately 90% NVO for tars and 50% for oils but only 5% of the coal is converted to tars. Because these tars and oils are not recycled, total toxicity of the raw product gas stream remains relatively low.

Results observed in the Ames Salmonella Assay of NVO fractions of HYGAS samples (Table 3) show that the greatest specific mutagenic activity is in the low temperature reactor condensate. Its specific mutagenicity is about 15% of the known carcinogen benzo(a)pyrene (BaP), but material balance studies have shown that not all of this mutagenicity leaves the gasifier. The most important HYGAS stream, the recycle oil, has an average NVO mutagenic activity less than 3% of BaP. Low or insignificant specific mutagenicity is observed with quench waters from the pretreater and gasifier and no mutagenicity could be detected in the spent char. Extrapolated specific mutagenicity of all process streams is less than 1 revertant/μg.

TABLE 3. MUTAGENICITY OF HYGAS PROCESS STREAMS (AMES SALMONELLA ASSAY)

Sample	Mutagenicity, rev/μg NVO Fraction	Process Stream
Recycle Oil	7	0.17
Pretreater Quench Water	2.4	0.007
Gasifier Quench Water	0.7	0.0005
Low Temperature Reactor Condensate	35	0.37
Spent Char	<0.1	neg.
Benzo(a)pyrene	260	

Cytotoxicity and genotoxicity measurements in mouse myeloma cells support the general conclusion that on a process stream basis toxicity is low. However, untreated quench waters contain significant toxicity (Table 4). They are the most toxic sample type, being threefold more genotoxic than LTR condensates or recycle oil. This test does not require metabolic activation but when the LTR condensate is activated with rat liver S9 enzymes, genotoxicity increases tenfold and approximates the relative activity of LTR condensate to BaP seen in the Ames Assay.

TABLE 4. TOXICITY OF HYGAS PROCESS STREAMS (MOUSE MYELOMA CELLS)

Sample	Cytotoxicity* L/g	Genotoxicity** L/g
Recycle Oil	16.5	15.5
Pretreater Quench Water	19.3	31.4
Gasifier Quench Water	55.7	47.3
Low Temperature Reactor Condensate	12.3	17.7
Methyl Methane Sulfonate	36.0	370
Low Temperature Reactor Condensate with Activation	20.8	175
Benzo(a)pyrene with Activation	112	1230

*The reciprocal of the NVO concentration for 50% growth inhibition.

**The reciprocal of the NVO concentration for a twofold increase in sister chromatid exchanges.

In the RAM assay HYGAS materials are approximately equivalent within a given end point (Table 5). There is however a clear indication of subtle toxicity (functional loss) at concentrations of HYGAS materials significantly lower than those required for cell killing.

TABLE 5. TOXICITY OF HYGAS PROCESS STREAMS (RAM ASSAY)

Sample	Cytotoxicity* L/g NVO	Functional Impairment** L/g NVO
Recycle Oil	7.1	9.8
Gasifier Quench Water	4.1	10.8
Pretreater Quench Water	6.1	8.1
Low Temperature Reactor Condensate	7.4	11.4
Vanadium Oxide	153	208

*The reciprocal of the NVO concentration for 50% cell killing.

**The reciprocal of the NVO concentration causing a 50% reduction in the phagocytic activity of viable cells.

Ocular toxicity tests in rabbits have demonstrated that recycle oil NVO is a severe irritant according to National Academy of Science criteria (NAS publication 1138, 1977). We observed inflammatory reactions, corneal ulcers, and panus that persisted for 21 days. Likewise, rabbit skin exposure results in mild to severe inflammatory reactions with some skin necrosis. Marked skin hypersensitivity is detected in guinea pigs. We found that raw recycle oil is a mouse skin carcinogen, inducing tumors in SKH hairless mice following chronic exposure (weekly 150 µl doses). The tumorigenic response is considerably less than that for BaP (.03 µg/week); however, 105 µg of the recyle oil NVO approximates the BaP tumor response. Tumor response is based on gross observation, but histologically confirmed squamous cell carcinomas of the skin have been observed, some with metastatic nodules. Thus while it is clear that recycle oil is toxic, it is important to emphasize that the potential for human exposure is limited. The nature of the stream and normal industrial hygiene protocols should make hazards associated with recycle oil totally manageable.

Table 6 gives preliminary toxicological evaluations of GFETC tars and oils. Results are for unfractionated samples and should not be confused with the toxicity of NVO fractions. Mutagenicity is insignificant in oils but present at a level 5% that of BaP in tars. Samples are cytotoxic and genotoxic but again not at high levels. The toxicity of untreated process water while relatively low is significant when the large volume of this stream is considered (Table 2).

TABLE 6. TOXICITY PRESENT IN THE GRAND FORKS ENERGY TECHNOLOGY CENTER'S SLAGGING FIXED-BED GASIFIER PROCESS STREAMS

	Tar	Oil	Water	Reference* Standards
Mutagenicity, rev/ g	4	<1	0	260
Cytotoxicity*, L/g	11	11	0.7	36
Genotoxicity*, L/g	16	12	1.4	370
Functional loss*, L/g	14		9	208

*As in assay of HYGAS samples, see Tables 3-5.

AIR MONITORING

The organic vapor concentrations we observed in the GFETC gasifier facility ranged from approximately 1-500 $\mu g/m^3$ for individual components with an overall organic vapor concentration of from 2-3.5 mg/m^3. One- to three-ring aromatic hydrocarbons accounted for the bulk (50-70%) of the material with aliphatic hydrocarbons (30-40%) accounting for most of the remainder. Phenols and heterocyclic compounds each accounted for about 2% of the total organic fraction. The concentrations of individual compounds (e.g., benzene) were well below TLV limits in all cases.

The bulk of the particulate-associated trace organic material was associated with particles having an aerodynamic size of ≤ 3.1 µm. The particulate phase organics contained significantly higher proportions of aliphatic and phenolic compounds than the vapor phase samples and this is consistent with published data for ambient air. Particle morphologies resembled those of lignite fly ash from combustion, and particle types included smooth spheres, vesicular spheres, agglomerated masses and crystalline fragments. Trace element size distributions were bimodal and resembled those for ambient air. Lead particle sizes were predominantly submicron, while particles of Al, Fe, and other crustal species were mostly of supermicron size. Aluminum-based aerosol enrichment factors calculated from Indian Head lignite showed that the composition of the aerosol resembled that of the coal, with the exception of modest enrichment of Mg, Na, As, and Pb in the submicron size range. Aerosol enrichment factors based on the earth's crustal composition were somewhat greater than those based on coal composition for several elements, suggesting potential errors in using crustal enrichment data to investigate chemical fractionation during aerosol formation.

CHARACTERIZATION OF TOXIC COMPOUNDS

Because toxicity was confined to nonvolatile materials, it was possible to fractionate and concentrate without evaporative loss of toxic material. As previously mentioned, the components of recycle oil were fractionated by acidity and polarity. Separation by polarity was accomincreasing proportions of benzene, accounted for half of the sample weight but were only slightly mutagenic despite the fact that they contained polyaromatic hydrocarbons such as BaP. Virtually all of the mutagenicity recovered was contained in the fourth most polar fraction, (eluted with methanol).

In the initial pH fractionations, methylene chloride samples were partitioned between an aqueous acid or base. The base fraction contained more than 70% of the recovered mutagenicity. Although the base fraction contained only 4% of the initial weight, its specific mutagenicity was more than tenfold higher than that of the original sample. The neutral fraction contained the remainder of the recovered mutagenicity with the acid fraction (exclusively phenolic) being nonmutagenic. The neutral and acidic fractions accounted for 50% and 30% of the initial weight, respectively.

Chemical analysis showed that the base fraction contained azaarenes (AA) and primary aromatic amines (PAA) in the ratio of 4:1. Since members of both classes of compounds are known to be toxic, further analyses were performed to determine which components were mutagenic. The loss of mutagenicity following mild nitrous acid treatment (which modifies PAA but not AA) suggests that the PAA are responsible for the mutagenicity. More conclusive evidence was obtained by applying a new procedure for cation exchange high performance liquid chromatography (8). This procedure separates PAA (weaker bases) from AA and resolves members of each class having pK_a values differing by less than 0.2 pK_a units. Chromatography of the LTR base fraction revealed that most of the mutagenicity is concentrated in a few fractions containing 2- to 4-ring PAA as demonstrated by GC/MS. Azaarenes which elute in the later fractions contain little of the mutagenicity.

CONCLUSIONS

The results of this study on the toxicological and chemical characterization of two high-BTU coal gasification pilot plants demonstrate that while toxicants are present, they are a minor component of the process streams. The toxicity is largely confined to the nonvolatile components of the by-product tars and oils. These materials will not leave the commercial plant site because they are ultimately consumed in the process. On-site emissions can be controlled through appropriate control technology. Occupational exposures can be minimized through effective industrial hygiene procedures. These considerations allow the general assessment that no apparent serious health or environmental problems are associated with coal gasification.

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GASEOUS FUGITIVE EMISSIONS FROM SYNFUELS PRODUCTION - SOURCES AND CONTROLS†

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ABSTRACT

Fugitive emissions are generally defined as emissions that are not released through an enclosure such as a duct or vent pipe. This definition includes sources of fugitive particulate emissions and sources of gaseous fugitive emissions. In this paper, the potential sources and control options for gaseous fugitive emissions from synfuels production facilities are described. Gaseous fugitive emissions are caused by process fluid leakage from seals (valves, pumps, flanges), process fluid purges (sampling, equipment cleaning), and secondary emission sources (drains, wastewater systems, cooling towers). The majority of sources of fugitive emissions in the U.S. are currently found in petroleum production and refining facilities, organic chemical manufacturing plants, and coke by-product plants. Synfuels production facilities will also have fugitive emission sources.

Fugitive emission regulations have been applied to California petroleum refineries for several years and U.S. New Source Performance Standards (NSPS) are currently under development for several industries. These regulations are based on the need to reduce emissions of volatile organic compounds (VOC), because VOC are photochemical ozone precursors. Some fugitive emissions also need to be controlled because compounds released in the emissions may be harmful. U.S. National Emission Standards for Hazardous Air Pollutants (NESHAP) have been developed for controlling fugitive emissions of vinyl chloride and benzene. Fugitive emissions from synfuels production facilities may require control because they contribute to atmospheric ozone formation and/or because the emissions contain harmful compounds. The nature of potentially harmful compounds will be dependent on variables such as the type of process, feedstock characteristics, and operating parameters.

Fugitive emission controls can be categorized as either work practices or engineering controls. Work practices include leak detection/leak repair programs and "housekeeping" practices. Leak detection and repair programs involve periodic testing to locate significant leaks and subsequent repairs to reduce or eliminate the leakage. Housekeeping practices would include procedures to minimize process fluid spills and to expedite spill cleanup. Engineering controls are generally equipment substitution strategies. For example, closed loop sampling connections eliminate process fluid purge emissions, and double mechanical pump seals can be operated to minimize seal

emission potential. These types of equipment could be substituted for equipment with a greater potential to leak process fluids.

Because the emission sources (pumps, valves, flanges, etc.) in synfuels plants will be similar to those in existing U.S. industries, emission control techniques used in existing industries will also be applicable to synfuels facilities. The experience that has been gained in applying fugitive emission controls will be valuable in developing emission control strategies for synfuels plants.

INTRODUCTION

Gaseous fugitive emissions are the result of process fluid leakage and process fluid purges. Secondary emission sources such as cooling towers and wastewater systems may also be classified as fugitive emission sources. In contrast to process emissions, which are released through ducts or vent pipes, fugitive emissions are released from numerous discrete sources such as valves, pumps, and flanges located throughout a process unit. Process emissions are amenable to application of emission control devices that either recover or destroy the emissions conveyed to the device by a duct or pipe, but fugitive emission sources require a completely different type of emission control strategy. The purpose of this paper is to identify the potential sources of gaseous fugitive emissions in synfuels production facilities and to discuss the types of controls that can be applied to reduce emissions from those sources.

Fugitive emissions have received rapidly increasing attention in the last five years and there are several reasons for this increased awareness of a need to control fugitive emissions. Because process emissions are released through an enclosed pipe or duct, it is fairly straightforward to convey these emissions to a control device. Furthermore, process emission sources generally contribute a much larger portion of the total emissions compared to fugitive emission sources. For these reasons, process emission sources have been selected for application of controls first. As more controls are applied to process sources, fugitive emissions become a significant contributor to the remaining controllable emissions from a process unit. In addition, fugitive emission sources may be the major contributor to the total emissions of specific compounds that require control.

The compounds released from fugitive emission sources may require control because they are volatile organic compounds (VOC), which have been linked to photochemical atmospheric ozone formation. Other compounds such as benzene and hydrogen sulfide may require control because the compounds themselves are health hazards. Regulations to control fugitive emissions have been applied to the petroleum industry in California for VOC control for several years, and other states are developing regulations. Federal New Source Performance Standards (NSPS) are currently being developed for VOC control in several industries. National Emission Standards for Hazardous Air Pollutants (NESHAP) have been developed for fugitive emissions of benzene and vinyl chloride. These regulatory activities have resulted in increased awareness of the need to learn more about the sources and controls of fugitive emissions.

SOURCES OF FUGITIVE EMISSIONS

Fugitive emissions are caused by process fluid leakage, process fluid purging and atmospheric exposure of process fluids by secondary emission sources. Any type of process equipment that is capable of allowing process fluids to come in contact with the atmosphere is a potential fugitive emission source. These sources of fugitive emissions are shown in Table 1.

PROCESS FLUID LEAKAGE

Sources of process fluid leakage include valve packings, seals on pumps, compressors and agitators, flange gaskets, relief valve seats, and valve seats on open-ended lines. An open-ended line is defined as a process valve that is installed with one side of the valve in contact with process fluid and the other side in contact with the atmosphere, such as purge valves, drain valves and vent valves.

All process valves, except relief valves and check valves, are activated by a valve stem which may have either a rotational or linear motion, depending on the specific design. The moveable stem requires a sealing element to resist fluid leakage while permitting movement of the stem. In most valves, this seal is achieved with a packing compression gland. Other valves may have elastomeric O-rings or grease-filled lantern rings to prevent leakage of process fluid. Although these types of seals are satisfactory for preventing gross leakage of process fluids, they can allow a significant amount of fugitive leakage. Corrosive or toxic process fluids may require the use of a valve with a diaphragm or flexible bellows to isolate the stem sealing element from the process fluid, and these valves would also provide increased resistance to fugitive leakage.

Packed seals on pumps, compressors, and agitators are similar to packed seals on valves. Because the shafts on these devices rotate constantly, periodic adjustment of the packing is required. Mechanical seals consist of stationary and rotating elements that are machined to a very close tolerance. The mechanical contact of the two elements resists fluid leakage. As with packed seals, leaks can occur where the shaft protrudes through the seal. Double mechanical seals and oil film seals have a barrier fluid system that resists seal leakage. However, seal leakage can be entrained in the oil system and can be released to the atmosphere by degassing from the oil reservoir.

Leaks from flange gaskets can be caused by loose bolts, improper specification of materials, thermal stresses, and deterioration of the gasket material. Although they are the most numerous type of fugitive emission source, flanges contribute a small portion of total fugitive emissions.

Relief valves are designed to open at a predetermined pressure in order to protect process equipment from damage due to overpressure. The discharge that occurs when these valves open is considered a process emission. Fugitive emissions from relief valves are the result of leakage through the valve when it is closed. This leakage can be caused by improper reseating after an

TABLE 1. FUGITIVE EMISSION SOURCES

Source Type	Location of Emission Release
Sources of Fluid Leakage	
Valves	Stem/body junction
Pumps and Agitators	
Packed seals & single mechanical seals	Shaft/case junction
Double mechanical seals	Shaft/case junction; oil reservoir degassing vent
Compressors	
Packed seals & single mechanical seals	Shaft/case junction
Double mechanical seals & oil film seals	Shaft/case junction; oil reservoir degassing vent
Flanges	Face/gasket junction
Relief Valves	Disc/seat junction
Open-ended lines (valves)	Valve disc/seat junction
Sources of Process Fluid Purges	
Sampling Operations	Purge/atmosphere contact
Equipment Emptying Operations	Purge/atmosphere contact
Secondary Emission Sources	
Cooling Towers	Cooling tower plume
Wastewater Systems	Drains, open sewers or canals, collecting basins, separators, aeration ponds.

overpressure, deterioration of the valve seat, and operation of the process at or near the set pressure that causes the valve to open.

Open-ended lines are found on valves used for draining equipment, for purging or venting equipment, and for obtaining process fluid samples. A faulty valve seat or incomplete closure of the valve would allow process fluid to leak to the atmosphere through the open-ended line.

PROCESS FLUID PURGES

The sources of process fluid purges are sampling operations and equipment draining and venting operations. In order to obtain a representative sample of process fluid, the sample line is purged with the process fluid. If this purge is allowed to contact the atmosphere, fugitive emissions may be created. Process fluids are also purged from equipment prior to removing the equipment from service for inspection, repair, replacement, etc. Atmospheric contact with these purges can also result in fugitive emissions.

SECONDARY EMISSION SOURCES

Cooling towers and wastewater systems are considered as secondary sources of fugitive emissions because they are not the initial source of the process fluids. Process fluids may enter a cooling tower water system due to leakage in heat exchangers or from the use of contaminated process water as cooling tower make-up water. As the contaminated water is circulated through the cooling towers, process fluid components are stripped from the water and are released to the atmosphere with the evaporated cooling water.

Wastewater systems consist of drains, collection basins, canals, separators, and water treatment facilities. Because these systems have numerous locations where the wastewater contacts the atmosphere and the wastewater is frequently in a state of turbulent mixing, process fluids in the wastewater can readily become atmospheric fugitive emissions.

SEVERITY OF FUGITIVE EMISSIONS

The degree of environmental severity associated with fugitive emissions is dependent on two variables: 1) species emitted and 2) the total emission rate. The relative importance of these variables depends on the type of environmental impact that is being evaluated. With respect to the impact of fugitive emissions on atmospheric ozone formation, the total emission rate of VOC is the most significant consideration. Impacts on industrial hygiene would be dependent on the types of substances emitted and the proximity of emission release points to workers. Some of the less volatile process fluids may also accummulate over a period of time, and workers may come into contact with harmful species at any time after the initial release of the process fluid.

The contribution of fugitive emission sources must also be accounted for in considering the need for Prevention of Significant Deterioration (PSD) review due to emissions in excess of De Minimis levels. The provisions of 40

CFR 51-52 allow exemption from PSD review if the annual controlled pollutant mass emission rate from a plant is less than the established De Minimis value.

Emission control cost effectiveness is closely related to the total number of sources and the emission factor for each type of source. It is less expensive to control a few sources with high emission rates than to control many sources with low emission rates, although the total uncontrolled emission contribution of the two groups may be equal.

ASSESSMENT OF POTENTIALLY HARMFUL SPECIES

One of the first criteria that can be used in evaluating pollutants of concern in the process stream is to identify compounds covered by existing regulations. These would include "criteria pollutants" covered by National Ambient Air Quality Standards (NAAQS, 40 CFR 50) and "regulated pollutants" covered by National Emission Standards for Hazardous Air Pollutants (NESHAP, 40 CFR 61). Some compounds of potential environmental concern may be present in synfuels streams, but have not been the subject of specific regulations. Such cases arise when there are insufficient or inconclusive data available for the promulgation of enforceable regulations. One method of identifying those compounds that need additional evaluation is to compare their Multimedia Environmental Goals (MEG's).

Multimedia Environmental Goals (MEG's) have been established for over 650 chemical substances and physical agents (e.g., noise, heat). These goals (in air, water, and solid waste streams) are the maximum discharge concentrations (DMEG's) and maximum ambient concentrations (AMEG's) which will avoid potentially hazardous risks for public health or the ecology. These goals are intended to be used in prioritizing research efforts, not in establishing discharge limits. Most of the MEG's are derived using models that translate toxicological data (threshold limit values, water quality criteria, carcinogen test results, etc.), dispersion assumptions, and federal standards or criteria into discharge and ambient level goals. In many cases the models translate data from one medium to goals for another medium. Despite their obvious limitations, the MEG's do provide a method (and often the only method) of identifying pollutants of potential concern.

In order to prioritize the need for concern about specific substances, their MEG values can be compared. In Table 2, maximum ambient concentrations (AMEG's) are shown for several species that could be present in synfuels process streams. The AMEG values are in micrograms of pollutant per cubic meter of ambient air; however, the actual numerical values are not directly applicable to fugitive emission sources. These AMEG values are shown here in order to give an indication of what ambient concentrations may be of concern for some species which may be present in synfuels plant fugitive emissions.

Except for the benzene and vinyl chloride NESHAP, fugitive emission regulations have been developed in the U.S. because of the need to reduce VOC emissions. Synfuels facilities will also have sources of fugitive VOC emissions and the presence of harmful species in these fugitive emissions will

TABLE 2. HARMFUL SPECIES POTENTIALLY PRESENT IN SYNFUELS PROCESS STREAMS

Pollutant	AMEG*
Sulfur Compounds	
Hydrogen sulfide	36
Carbonyl sulfide	800
Carbon disulfide	143
Mercaptans	2.4
Thiosulfates	-
Nitrogen Compounds	
Ammonia	43
Cyanides	26
Thiocyanates	-
Nitrates, Nitrites	-
Organic Compounds	
Carbon monoxide	10,000
Benzene and other aromatics	7.1
Polynuclear aromatics (PNA's)	0.00005 to 119
Phenols	24 to 45
Organometallic compounds	-
Methanol	619
Trace Metals	
Antimony	1.2
Arsenic	0.005
Beryllium	0.01
Cadmium	0.02
Lead	0.36
Mercury	0.01
Nickel	0.035
Selenium	0.03

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* Ambient Multimedia Environmental Goal ($\mu g/m^3$) from References 1, 2, and 3.

depend on the type of process, feedstock characteristics, and operating conditions. In the first phase of an environmental assessment program, the major process discharge streams are characterized. Except for the fugitive emission sources that contain (and therefore have the potential to emit) the species in these discharge streams, very little of this characterization is applicable to fugitive emissions. Because fugitive emissions are composed of the process fluid, it is necessary to know what harmful species are in these process fluids. Process stream characterization data for synfuels processes are frequently unavailable, especially for developing technologies. This information may be deemed proprietary by the process developer because the purpose of most of these process stream analyses is to determine the effects of process variables on the yield of the primary reaction products, not to characterize potentially harmful species in the streams.

Although limited test data are available, it is possible to estimate the harmful species that are likely to be present in a process stream. In Table 2, several general categories of harmful substances that could be found in synfuels processes are shown. This list does not include all possible harmful compounds, and each type of process would have a different distribution of harmful species. Some general conclusions can be reached when comparing different types of synfuels processes. For example, a process that produces organic liquids either as primary products or as by-products is more likely to have some streams containing phenols, aromatics, and polynuclear aromatics (PNA's) compared to a process that produces only a gaseous product primarily composed of carbon monoxide and hydrogen. Since trace metals are introduced into the synfuels processing facility in the coal feedstock, analysis of the feedstock would show which elements need to be considered for a particular feedstock.

ASSESSMENT OF EMISSION RATES

The average emission rate for a particular type of source is called the emission factor. The total number of sources multiplied by the emission factor equals the total emission rate from that type of source. For assessment of the severity of VOC emissions, the total emission rate is the main factor to consider. Other factors become significant when evaluating VOC emission control strategies, as discussed in the section on fugitive emission controls.

The total emission rate of harmful species is also important, but the emission rate of individual sources may also be significant. The effect on the environment beyond the boundaries of the synfuels plant is primarily determined by the total emission rate from the plant, but industrial hygiene considerations within the plant boundaries are also dependent on individual emission factors for sources. For example, if a particular type of source has a very high emission factor but there are very few sources present, the emission contribution may be a small fraction of the total hazardous fugitive emissions from the plant. However, if plant workers are frequently required to be in close proximity to this type of source, additional emission controls or protective equipment for workers may be needed.

Each synfuels process will have unique characteristics, and therefore process-specific (or even site-specific) evaluation of the severity of fugitive emissions will be necessary. Extensive fugitive emission testing has been conducted in petroleum production and refining facilities, coke by-product plants and organic chemical plants in the U.S., and a limited fugitive emission test has been performed at a European coal gasification plant (Ref. 4). The results of these tests show that emission factors for the same type of source (valve, pump, flange) can vary over several orders of magnitude for different types of processes, and significant variations exist for the same type of process at different locations. Because of this variability, it is difficult to estimate emissions from one type of process based on data obtained from a different process. The primary benefit that these tests results provide for synfuels processes pertains to development of emission control strategies as described in the section on fugitive emission controls.

Because of the two types of tests that can be performed, there are two types of results that are generated in fugitive emission testing; leak screening and leak rate measurement. Leak screening consists of a method to identify the relative magnitude of leakage from fugitive emission sources. Leak rate measurement involves enclosure of a leaking source and measurement of the pollutant mass emission rate from the source. These two types of testing results can be combined to develop emission factors. In Table 3, emission factors are shown for fugitive emission sources in several industries. These emission factors have units of kilograms per day per source. Therefore, the total emissions from a particular type of source can be estimated by multiplying the number of sources by the emission factor.

In Table 3, the 95 percent confidence intervals for the emission factors are also shown. It is important to consider these confidence intervals since they indicate that the true emission factor is expected to be found within these confidence intervals 95 percent of the time. If confidence intervals (for different sources or processes) overlap, it is not possible to state that the true emission factors for the different sources or processes are significantly different.

In addition to their contribution to emissions of harmful substances, fugitive emissions also need to be included in De Minimus calculations. If the total controlled emission rate from a plant exceeds the De Minimus level for a particulate pollutant, PSD review is required. De Minimus levels for several pollutants are shown in Table 4 in metric tons (Mg) per year. As an example of how fugitive emissions might contribute to De Minimus levels, the total hydrocarbon and carbon monoxide emission rates estimated for the Kosovo coal gasification plant are shown in Table 5. Hydrocarbon emissions of 5.72 kg/day would be 2.1 metric tons/year, which is approximately 6 percent of the De Minimus level of 36 tons/year of volatile organic compounds.

FUGITIVE EMISSION CONTROLS

Fugitive emission controls can be categorized as either work practices or engineering controls. Work practices are specific work activities whose objective is to prevent emissions, to reduce the potential for emissions, to

TABLE 3. COMPARISON OF EMISSION FACTORS

Source Type Service	Emission Factor (95% confidence interval) for Various Types of Industrial Processes (kg/day-source)					
	Kosovo coal gasification plant*	Organic Chemicals Manufacturing**			Refineries***	Natural Gas Plants****
		Vinyl Acetate	Cumene	Ethylene		
Valves						
Hydrogen	-	-	-	-	.20(.076,.49)	-
Gas/Vapor	.0019(.0002,.016)	.05(.011,.33)	.12(.033,.54)	.26(.087,.76)	.64(.33,1.2)	.48(.2,1)
Light Liquid	.0026(.0008,.01)	.0033(.001,.022)	.061(.022,.22)	.22(.076,.65)	.26(.18,.39)	
Heavy Liquid		-	-	-	.0054(.0022,.016)	-
Aqueous	.0012(Neg*****,.12)	-	-	-	-	-
Pumps						
Light Liquid	.005(.009,.03)	.047(.001,1.1)	.57(.011,2.9)	.75(.065,8.7)	2.7(1.7,4.0)	1.5(.5,4)
Heavy Liquid		-	-	-	.50(.21,1.2)	-
Aqueous	.0012(Neg,.0021)	-	-	-	-	-
Compressors						
Hydrogen	-	-	-	-	1.2(.54,2.5)	-
Gas/Vapor	-	-	-	-	15(7.2,32)	4.9(.7,30)
Flanges	.00036(Neg,.02)	-	-	-	.0061(.0022,.027)	.026(.01,.05)
Open-ended lines	-	-	-	-	.054(.017,.17)	.53(.2,1)
Relief Valves	-	-	-	-	2.07(.76,5.3)	4.5(.1,100)
Drains	-	-	-	-	.76(.25,2.2)	-

* Total hydrocarbons from Reference 4
** Nonmethane hydrocarbons from Reference 5
*** Nonmethane hydrocarbons from Reference 6
**** Total hydrocarbons from Reference 7
*****Negligible = $<3 \times 10^{-5}$ kg/day-source

TABLE 4. DE MINIMIS LEVELS TRIGGERING PSD REVIEW

Pollutant	De Minimis Level* metric tons/yr
Carbon monoxide	91
Nitrogen oxides	36
Sulfur dioxide	36
Ozone	36 (as volatile organic compounds)
Lead	0.5
Asbestos	0.006
Beryllium	0.0004
Mercury	0.09
Fluorides	2.7
Sulfuric acid mist	6
Hydrogen sulfide (H_2S)	9
Total reduced sulfur (including H_2S)	9

* 40 CFR 51-52.

TABLE 5. TOTAL EMISSION RATES FROM KOSOVO FUGITIVE EMISSION SOURCES (from Ref. 4)

Source Type/Service (Emission Factor - kg/day-source)	Process Unit											
	Rectisol		Phenosolvan		Tar Separation		Gas Cooling		Gasification		Total	
	Number Sources	Emissions	Number Sources	Emissions	Number Sources	Emissions	Number Sources*	Emissions	Number Sources**	Emissions	Number Sources	Emissions***
Hydrocarbon Emissions												
Valves/gas (0.0019)	169	0.32	37	0.07	33	0.06	85	0.16	99	0.19	423	0.80
Valves/hydrocarbon liquid (0.0026)	544	1.41	112	0.29	176	0.46	68	0.18	0	0	900	2.34
Valves/aqueous (0.0012)	78	0.09	209	0.25	56	0.07	0	0	140	0.17	483	0.58
Flanges/gas (0.00024)	558	0.13	133	0.03	151	0.04	263	0.06	355	0.09	1460	0.35
Flanges/hydrocarbon liquid (0.00048)	1459	0.70	494	0.24	524	0.25	292	0.14	0	0	2769	1.33
Flanges/aqueous (< 3×10^{-5})	208	<0.006	916	<0.03	165	<0.005	0	0	273	<0.008	1562	<0.05
Pumps/hydrocarbon liquid (0.005)	33	0.17	8	0.04	6	0.03	0	0	0	0	47	0.24
Pumps/aqueous (0.0012)	2	<.003	7	0.01	8	0.04	0	0	6	0.01	23	0.03
TOTAL	-	2.83	-	0.96	-	.92	-	0.54	-	0.46	-	5.72
Carbon Monoxide Emissions												
Valves/gas (0.0012)	169	0.20	37	0.04	33	0.04	85	0.10	99	0.12	423	0.51

* Based on two of three cooling trains in operation.
** Based on two of six gasifiers in operation.
*** Does not include emissions from open-ended lines, sampling purges, or wastewater systems.

identify emitting sources and to mitigate emissions from these sources. Engineering controls include equipment design, equipment operation, and equipment specification procedures that either reduce emission potential of sources or capture and control emissions from the sources. The effectiveness of fugitive emission controls can be dependent on many variables, and in some cases effectiveness cannot be assessed before applying the controls.

WORK PRACTICES

Work practices that can prevent or reduce the potential for fugitive emissions are sometimes called "housekeeping" practices. The procedures are implemented in all types of industrial plants in order to reduce safety and fire hazards, and they can also be applied to reduce fugitive emissions. Specific procedures regarding process fluid spills and spill cleanup can be used to minimize fugitive emissions from these sources. Fugitive emissions from equipment draining, purging and venting operations can be minimized by specifying procedures that prevent or reduce the emissions. Atmospheric contact with these process fluids may occur at the point of discharge from process equipment or in the wastewater systems. Process fluids that are drained, purged or vented from process equipment can be collected for recycle, disposal, or pollutant destruction instead of allowing the process fluids to become atmospheric emissions. Work practices that identify emitting sources and apply emission reduction techniques are generally referred to as leak detection and repair programs. Fugitive emission tests have consistently shown that a large fraction of total emissions are contributed by a small fraction of the total number of sources. Therefore, periodic repair or replacement of all sources would be a very inefficient approach to fugitive emission control. Leak detection methods provide a way to identify which sources are contributing the bulk of emissions and therefore warrant emission reduction efforts. Leak detection and repair programs can be applied to these sources of process fluid leakage: valves, pumps, compressors, agitators, flanges, relief valves, and open-ended lines.

Leak detection methods include individual component surveys, area (walk-through) surveys, and fixed-point monitors. They are described in this order because the first method is also included as part of the other methods. In the individual component survey, every fugitive emission source (pump, valve, compressor , etc.) is checked for evidence of process fluid leakage at regular intervals (monthly, quarterly, yearly, etc.). The method used to detect leakage may involve sensory examination, soap bubbles spraying, or instrument techniques. Liquid leaks, especially pump seal failures, can be readily detected visually, but the liquid leak may be water or other unimportant compounds. High pressure leaks may be audible, and leakage of odorous compounds can sometimes be detected by smell. These sensory techniques are only useful for identifying very large leaks.

An individual component survey using soap bubbles involves spraying a soap solution on the area of potential leakage and observing any bubble formation caused by a gaseous leak. This technique is fairly rapid and inexpensive, but it is not applicable to moving shafts, hot sources (above

100°C), cold sources (below 0°C), or sources where leaks of compounds other than pollutants could give a false indication of leakage.

Instrument techniques require the use of some type of portable pollutant detector. The probe of the detector is traversed around the potential leak areas, and an increase in the detected pollutant concentration identifies the leak. Various types of detectors can be used for an instrument survey. An appropriate "action level" or leak definition is chosen, and all sources that exceed this level are repaired or replaced in order to reduce the leakage from the source. In the development of fugitive emission regulations, the most commonly selected "action level" has been 10,000 ppmv. In Table 6, the percent of sources that would be expected to exceed this action level and require repair is shown for several types of sources in different industries. The results of a leak detection survey show which types of sources have the most significant leaks.

A walk-through survey involves periodic leak detection by using a portable pollutant detector for measurement of ambient pollutant levels in the process unit. Areas that are found to have elevated pollutant concentrations are then subjected to individual component surveys in order to locate the leakage sources for repair. Fixed-point monitors have permanent pollutant detectors operating throughout the process unit. If elevated pollutant levels are detected, individual component checks are used to find the sources needing repair.

Once a source has been identified as a leak requiring repair, appropriate action is taken to reduce or eliminate the leakage. Repair methods vary, depending on the type of source, and source replacement is also a repair option. Most pumps have spares that can be operated while the pump is out of service for repair. Many compressors do not have spares, and if the seal repair required a shutdown of the process unit, temporary emissions due to the shutdown could exceed the emissions from the seal if it was not repaired until the next scheduled shutdown. Leaks from packed seals or pumps, compressors, agitators, and valves may be reduced by simple tightening of the packing. Mechanical seals require removal from the equipment for repair or replacement. Grease injection in some types of valves may reduce leakage. Leaks from open-ended lines can be reduced by closing the valve seat more completely.

Leak detection and repair for cooling towers would require the use of periodic or continuous monitoring of pollutant concentrations in the cooling water. Elevated concentrations would indicate leakage, but individual process equipment such as heat exchangers would be difficult to pinpoint as the source of the leak.

ENGINEERING CONTROLS

Engineering controls involve the use of equipment that can capture and control emissions, or that prevents emissions. Each type of source requires assessment of operating conditions and constraints in order to determine which types of engineering controls are applicable.

TABLE 6. COMPARISON OF PERCENT OF SOURCES LEAKING

	Percent of Sources Leaking* for Various Types of Industrial Processes				
Source Type Service	Kosovo Coal Gasification Plant**	Organic Chemical Manufacturing***	Refineries****	Natural Gas Plants*****	Coke By-product Plants******
Valves					
Hydrogen	4	-	20.8	-	-
Gas/Vapor		11.4	12.6	16.4	-
Light Liquid	1	6.5	11.4		3.23
Heavy Liquid		0.4	0.2	-	-
Pumps					
Light Liquid	2	8.8	24.0	29.7	20.5
Heavy Liquid		2.1	3.8	-	-
Compressors					
Hydrogen	-	-	44.6	-	-
Gas/Vapor	-	9.1	57.0	52.8	8.8*******
Flanges	0.5	2.1	0.54	3.1	0.0
Open-ended lines	4	3.9	7.7	11.9	-
Relief valves	-	3.2	8.6	17.5	-
Drains	-	3.8	4.7	17.0	-

* Leaking defined as a screening value $\geq$10,000 ppmv
** from Reference 4
*** from Reference 5
**** from Reference 6
***** from Reference 7
****** from References 8, 9, and 10
*******Exhausters

Engineering controls for pumps include sealless pumps, double mechanical seals, and closed vent systems. Sealless pumps such as diaphragm pumps or "canned" pumps do not have a shaft/case junction that is exposed to process fluid. Therefore the potential to emit is eliminated, although these pumps have operating limitations that prevent universal application. Double mechanical seals consist of two mechanical sealing elements with a barrier fluid in a chamber between the seals. This barrier fluid system can be operated to purge into the process fluid to prevent leaks or to dissolve any seal leakage in the barrier fluid. Leakage dissolved in barrier fluids can be emitted by degassing from the barrier fluid reservoir. Closed vent systems can be used to transport pump seal leakage to a control device such as a combustion source or vapor recovery system. Closed vents can be connected to the oil reservoir degassing vent or to an enclosure fitted to the pump case in order to contain seal leakage.

Engineering controls for compressors are similar to those for pumps. In addition to double mechanical seals, some types of compressor seals may also have oil reservoir degassing vents that can be connected to closed vent systems. Many reciprocating compressors have closed vent systems to transport seal leakage to a safe release point. These vents can also be connected to control devices. Engineering controls for agitators are similar to those for pumps and compressors.

Fugitive emissions from relief valves can be controlled with rupture discs, resilient seat relief valves, and closed vent systems. A rupture disc upstream of the relief valve will prevent leakage through the valve seat, but the disc must be replaced after each overpressure release. Resilient seat relief valves may have superior ability to re-seat after overpressure release, compared to rigid seat relief valves, but no test data are available to verify this advantage. Closed vent systems are frequently used to transport relief valve discharges to recovery or disposal systems. These closed vent systems would also convey any fugitive leakage to the control device.

Leaks from open-ended lines are the result of leakage through a valve seat to the atmosphere via the open-ended line. These leaks can be minimized by installing a cap, plug, blind flange or another valve to the open-ended line. These devices would be opened only when the lines were put into service for draining or purging.

Process fluids that are purged from sampling connections can be controlled by using closed loop sampling systems. The closed loop system is operated such that the process fluid purge is either returned to the process or is collected in a closed vessel for eventual recycle or disposal.

Engineering controls for valves provide an internal barrier to prevent contact of process fluid with the valve stem. Diaphragm valves and bellows sealed valves have a moveable internal seal to resist leakage. Operating constraints limit the applicability of these types of controls.

Engineering controls for wastewater systems are primarily aimed at isolating the contaminated wastewater from the atmosphere. Drains with liquid traps prevent atmospheric contact with the drain system vapor space. Covers for wastewater separators and transport systems also reduce atmospheric contact. A closed vent system connected to the wastewater system vapor space would provide the best control potential, but would be difficult to apply.

CONTROL EFFECTIVENESS

Control effectiveness for fugitive emission controls is dependent on many variables. Some of those variables cannot be estimated before actually applying the control method. It is possible to estimate the maximum achievable control effectiveness, although actual effectiveness will probably be lower. Table 7 shows the estimated control effectiveness for work practice and engineering controls.

Leak detection and repair programs are subject to many variables. The frequency of inspection, leak definition, interval between leak detection and repair, repair effectiveness, occurrence rate, and recurrence rate are all related to the overall effectiveness of leak detection and repair programs. The costs and benefits of changing these variables will determine the optimum control strategy for each process unit. Limited repair studies for valves in the organic chemicals industry indicate that a 70 percent emission reduction can be achieved by using "directed maintenance". Directed maintenance requires use of the pollutant detection instrument during repair in order to determine the success of repair immediately. This method has been shown to be much more effective compared with undirected maintenance, where the repair is completed and then the source is re-checked for evidence of leakage.

The effectiveness of double mechanical seals can approach 100 percent if the barrier fluid is at higher pressure than the process fluid. Closed vent systems are dependent on the control efficiency of the device to which emissions are transported.

Rupture discs provide 100 percent control, but must be replaced after overpressure release or deterioration of the disc. Closed vents are connected to control devices capable of handling overpressure relief discharges. Depending on the turn down capability of the control device, effectiveness can range from 60 to 90 percent.

Because the controls for open-ended lines, sampling connections, and valves essentially eliminate the source of emissions, control effectiveness approaches 100 percent. The achievable control effectiveness for wastewater systems is difficult to estimate because each system is different and all systems are complex with numerous potential emission points.

CONCLUSIONS AND RECOMMENDATIONS

Synfuels production facilities will have the same types of fugitive emission sources that are currently found in U.S. petroleum production and refining facilities, organic chemical plants, and coke by-product plants.

TABLE 7. MAXIMUM POTENTIAL EFFECTIVENESS OF FUGITIVE EMISSION CONTROLS

Source Type Control Method	Control Effectiveness (percent reduction)
Valves, pumps, compressors, agitators flanges, open-ended lines, relief valves	
Leak detection/directed maintenance	70*
Pumps, compressors, agitators	
Double mechanical seals	100
Sealless equipment	100
Closed vent systems	90
Relief valves	
Rupture discs	100
Resilient seat valves	-**
Closed vent systems	60-90
Open-ended lines	
Caps, plugs, blinds, valves	100
Sampling connections	
Closed loop sampling	100
Valves	
Diaphragm/bellows seal	100
Wastewater systems	
Trapped drains	-**
Covered systems	-**
Closed vent system	90-100

* Based on test data for valves in organic chemical industry, Reference 11.
**Effectiveness not estimated

The magnitude and severity of fugitive emissions from synfuels facilities will be dependent on various factors, some of them process- or site-specific. Fugitive emission testing in U.S. industries has provided a basis for developing test strategies and control techniques for synfuels facilities.

Because the sources of fugitive emissions are the same, emission control techniques identified for U.S. industies should also be applicable to synfuels facilities. The applicability and control effectiveness of these controls will also require a case-by-case analysis for each facility. The developing nature of this industry in the U.S. provides an excellent opportunity to develop and evaluate fugitive emission controls throughout the development of a process from design to commercialization.

The most significant recommendations that can be made regarding fugitive emissions in the U.S. synfuels industry are related to control strategy development. As each technology develops, the process of providing fugitive emission assessment and control can also develop.

In the design phase of a process, streams that will require fugitive emission control can be identified. Design changes to minimize the number of sources or to make the sources accessible for inspection and repair can be initiated. As the process moves into the pilot plant stage, fugitive emission testing can be applied to estimate the severity of the problem and to identify areas where special emission control efforts are needed. During pilot plant operation, different types of engineering controls can be evaluated, especially for sources in severe service due to temperature, abrasive fluids, hazardous compounds, etc. Pilot plant experience can be valuable for evaluating seal lifetimes, repairability of sources, and other factors that determine the most cost-effective fugitive emission control strategy.

Evaluation of fugitive emission controls throughout the development of synfuels process should result in a well-defined, effective control strategy that will be implemented upon start-up of full-scale facilities. Proper assessment of hazards and cost effectiveness of controls will prevent delays in obtaining approval of emission controls for operating permits.

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CONTROL SYSTEMS FOR AIR EMISSIONS FROM COAL GASIFICATION

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ABSTRACT

This paper discusses control systems somewhat unique to coal conversion processes. The main subjects covered will be the control of emissions resulting from both the loading of gasification reactors and from the removal of acid gas from the raw process gas. Alternate control systems will be identified and difficulties in establishing Best Available Control Technology (BACT) will be addressed.

GASIFICATION REACTORS

Gasification reactors consist of primarily two types with regard to coal feeding: continuous and intermittent.

With continuous feeding, a coal slurry is usually the feedstock. Coal gasifiers utilizing slurry feeds are fed under pressure, thereby eliminating the need for a coal lock hopper. Air emissions from the gasifier feeding operation are eliminated, since the process occurs in a totally enclosed system.

With intermittent feeding, dry coal is usually the feedstock. This type of feeding requires the use of a coal lock hopper (Figure 1). The various operations required in intermittent dry coal feeding produce emissions that necessitate control to mitigate their environmental impact.

The sequence of the coal lock hopper operation consists of loading, isolating, pressurizing, unloading, isolating, depressurizing, and restarting the cycle. This cycle operates continuously, even though the coal is fed into the gasifier intermittently. To demonstrate this operation and the resultant emissions, assume that Step 1 begins when the coal dump has been completed and the bottom valve has been closed. At this point, the coal lock hopper is filled with reactor gas at reactor pressure. The next step in the cycle is the depressurizing of the coal lock hopper. These gases can be accumulated in a low-pressure vessel from which they may be transferred by compression to the product gas or fuel gas systems (Figure 2). When the vented gas is utilized as fuel gas, it must be treated to remove sulfur compounds before or after combustion due to its high sulfur content.

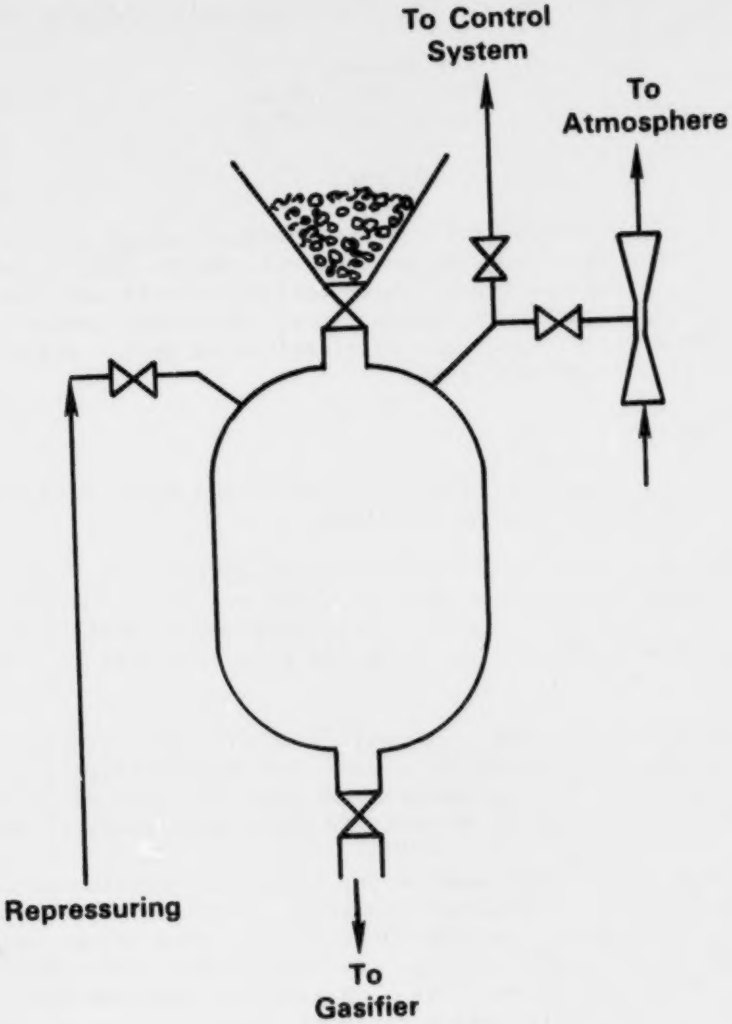
To Control System
To Atmosphere
Repressuring
To Gasifier

Figure 1. Coal Lock Hopper

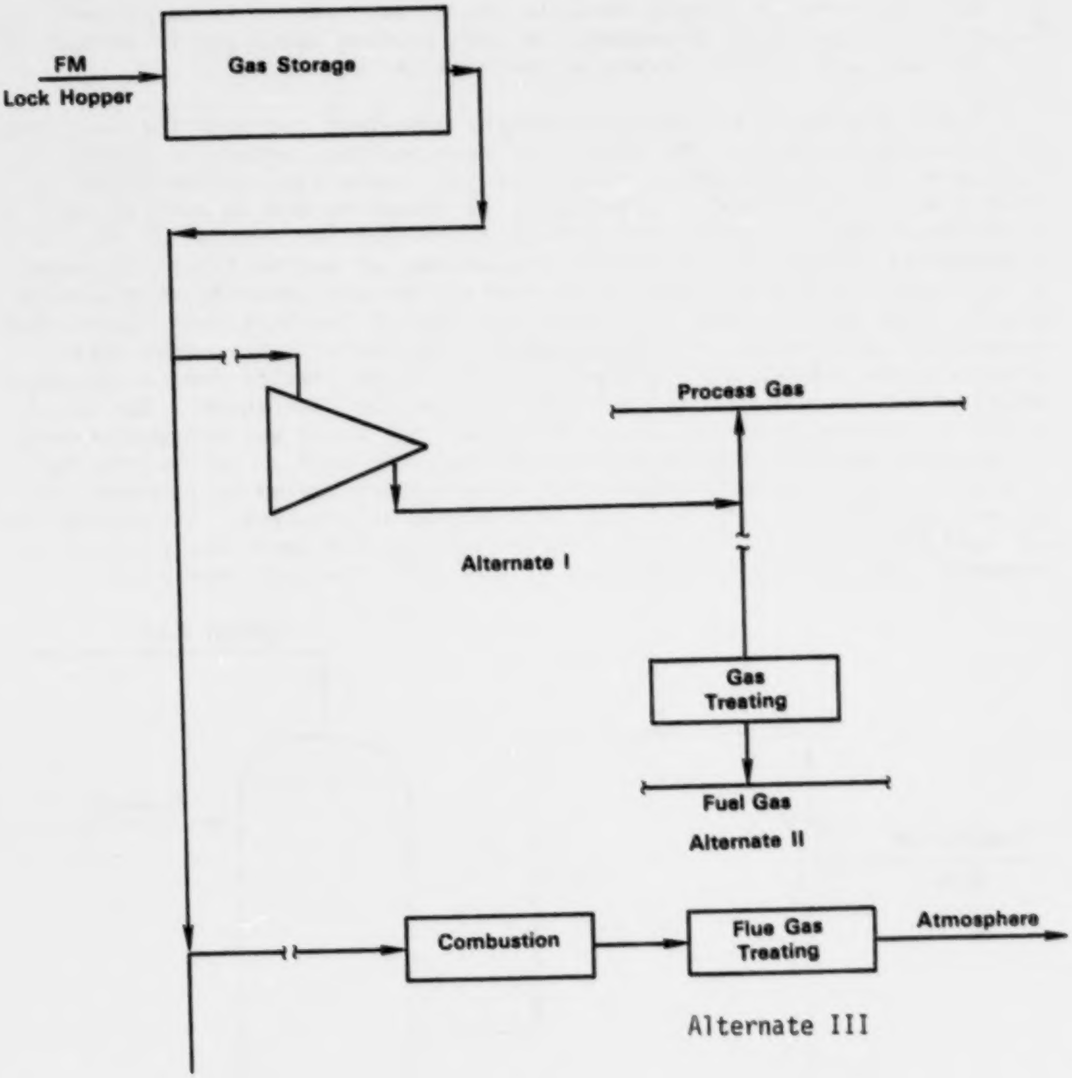
FM
Lock Hopper
Gas Storage
Process Gas
Alternate I
Gas Treating
Fuel Gas
Alternate II
Combustion
Flue Gas Treating
Atmosphere
Alternate III

Figure 2. Coal Lock Hopper Vent Gas Treating

An evacuation step is essential since the coal lock hopper can only be depressurized to slightly above atmospheric pressure. This step depletes the amount of gas remaining in the coal lock hopper and ensures that gas does not flow from the hopper when the upper coal feed valve is opened. Evacuation is continued throughout the coal loading operation to ensure that no explosive mixture occurs as the coal is introduced.

Three methods of air emission control have been proposed for handling the evacuated material. The first, and most popular, method is direct venting of the gas through an evacuation jet, since this stream would contain very little total contaminants. A second method is routing the discharge of the evacuation jet through a scrubber for removal of the contaminants (Figure 3). A loss of evacuation jet motive force can cause an explosive mixture to occur in the system, thereby creating an explosion hazard. Care must be take to prevent the risk of creating this hazard when evacuating gas from the coal lock hopper. The protection against this hazard creates expenditures which are difficult to justify due to the small amount of contaminants prevented from entering the atmosphere. The third method is pressurizing the coal lock hopper with inert gas and maintaining the pressure in the hopper above reactor pressure during the reactor coal feed cycle. This method necessitates an extensive system to compress the gas and introduce it into the coal lock hopper as required. Additional raw gas feed processing is needed to remove the recycled inert gas required to guarantee that reactor gas does not diffuse into the coal lock hopper.

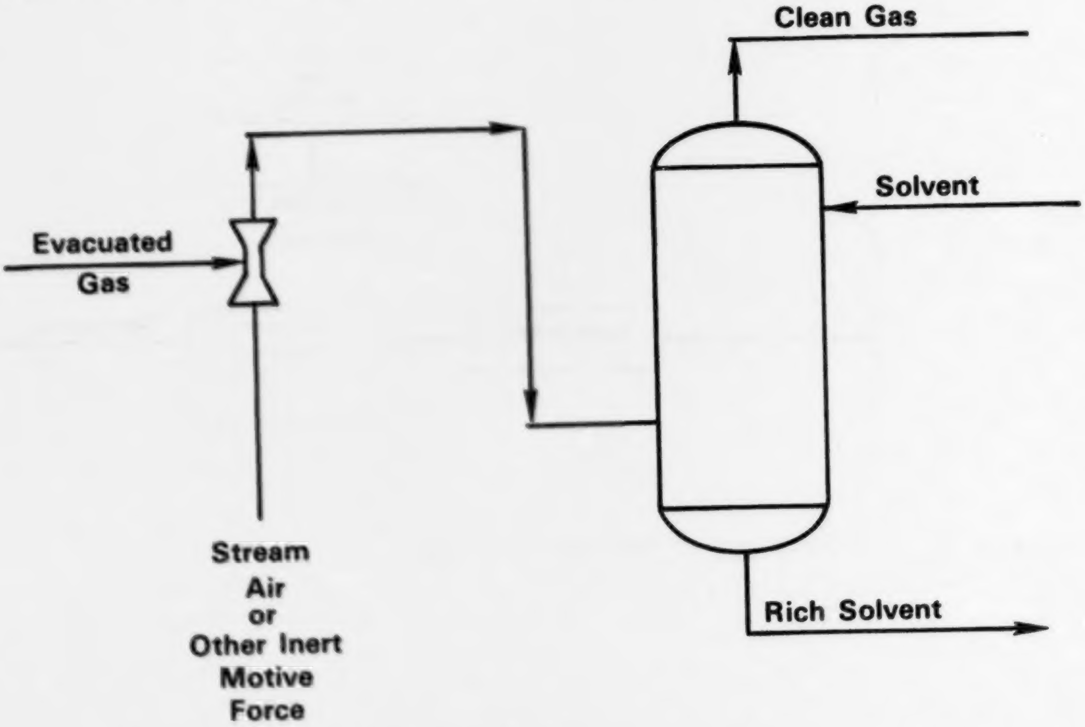

Figure 3. Treatment of Evacuated Gas

Table 1 compares the differences in emissions between the control system utilizing raw gas pressurizing and the control system utilizing inert gas pressurizing.

TABLE 1. EMISSIONS FROM COAL LOCK HOPPER

PRESSURIZING MEDIUM	RAW GAS		INERT GAS(1)
COAL TYPE:	NO. 6 ILLINOIS		NOT STATED
PLANT SIZE:	270 BILLION BTU/DAY		250 BILLION BTU/DAY
CONTROL SYSTEM:	UNCONTROLLED	98% RECOVERY	RECOVERY 400 PSIG→250 PSIG
EMISSIONS: (T/D)			
SULFUR	1,930	35	25
C_2 + HYDROCARBONS	3,160	70	4,000(2)
METHANE	21,160	429	

(1) EPA 450/2-78-012 Guideline Series.
(2) Listed as hydrocarbons.

RAW GAS TREATING

Competitive gas treating processes for H_2S and CO_2 removal from the raw gas stream are shown in Table 2.

TABLE 2. ACID GAS REMOVAL PROCESSES

Physical Absorption Processes	Solvent Used
· Rectisol	Methanol
· Purisol	N-methyl-2-pyrrolidone
· Selexol	Dimethyl ether of polyethylene glycol
· Fluor Solvent	Propylene Carbonate
· Estasolvan	Tri-n-butyl phosphate

Chemical Absorption Processes	Solvent Used
· MEA	Monoethanolamine
· Fluor Econamine	Diglycolamine
· Benfield	Potassium Carbonate Solution

The three processes receiving the most attention in the treating of raw gas from coal gasification are Rectisol, Purisol, and Selexol (Figure 4). Rectisol has the advantage in that it uses a methanol solvent which is

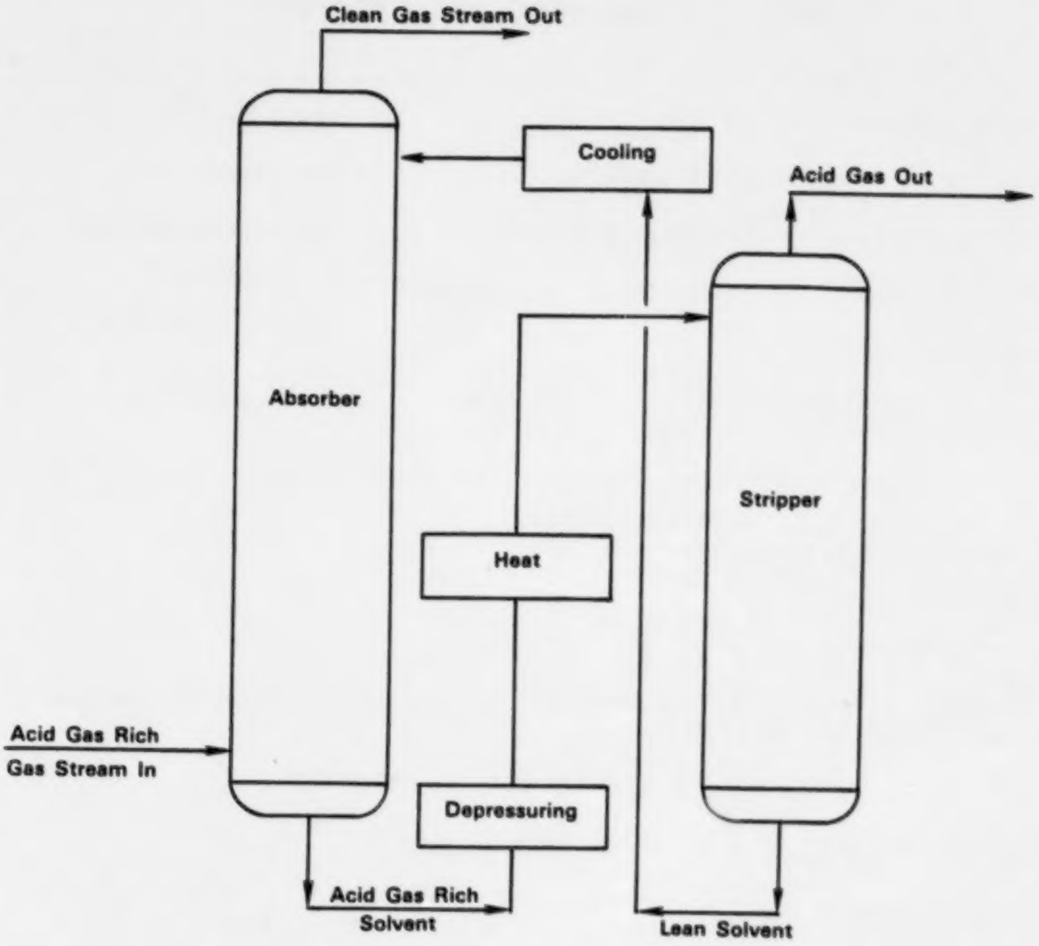
Clean Gas Stream Out
Cooling
Acid Gas Out
Absorber
Stripper
Heat
Acid Gas Rich
Gas Stream In
Depressuring
Acid Gas Rich
Solvent
Lean Solvent

Figure 4. Typical Gas Treating Process

manufactured in plants that produce synthol liquids and methanol. Results of research continuously being conducted improve the performance of existing processes and are used to derive new processes for the removal of acid gas. This research work may change the favorability of the processes.

These acid gas removal processes can be operated in two modes: selective and nonselective. In the selective mode, the acid gas is removed in two streams. One stream of CO_2 is highly concentrated with H_2S and the second stream contains small amounts of H_2S in the CO_2. The selective operating mode is accomplished by the use of either two absorption steps and two stripping steps or in one absorption step with two stripping steps. Unfortunately, at different operating conditions, none of the solvents removes all of the H_2S without a large amount of the CO_2 also being removed. For this reason, numerous processing operations must be considered for removal of sulfur compounds to prevent their escape to the atmosphere. Figures 5 through 14 demonstrate ten methods of removing sulfur compounds from the acid gas streams based on selective and nonselective modes of operation for the Rectisol Process. By utilizing the Selexol and Purisol Processes, 20 additional processing operations can be drawn and by shifting the processes into different positions, a number of other operations can be devised.

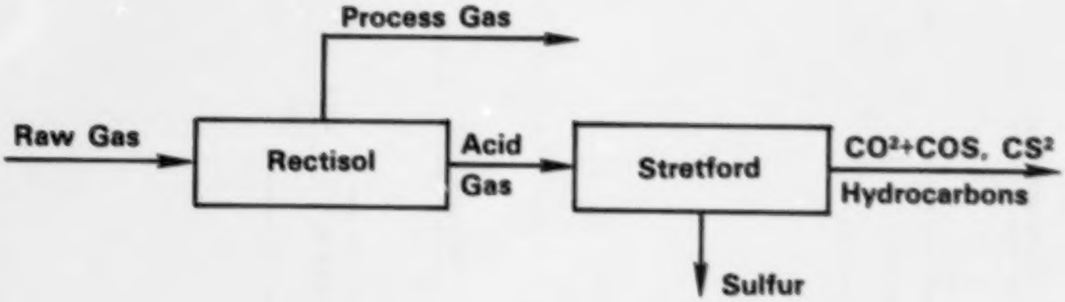

Figure 5. Raw Gas Treating Alternate I

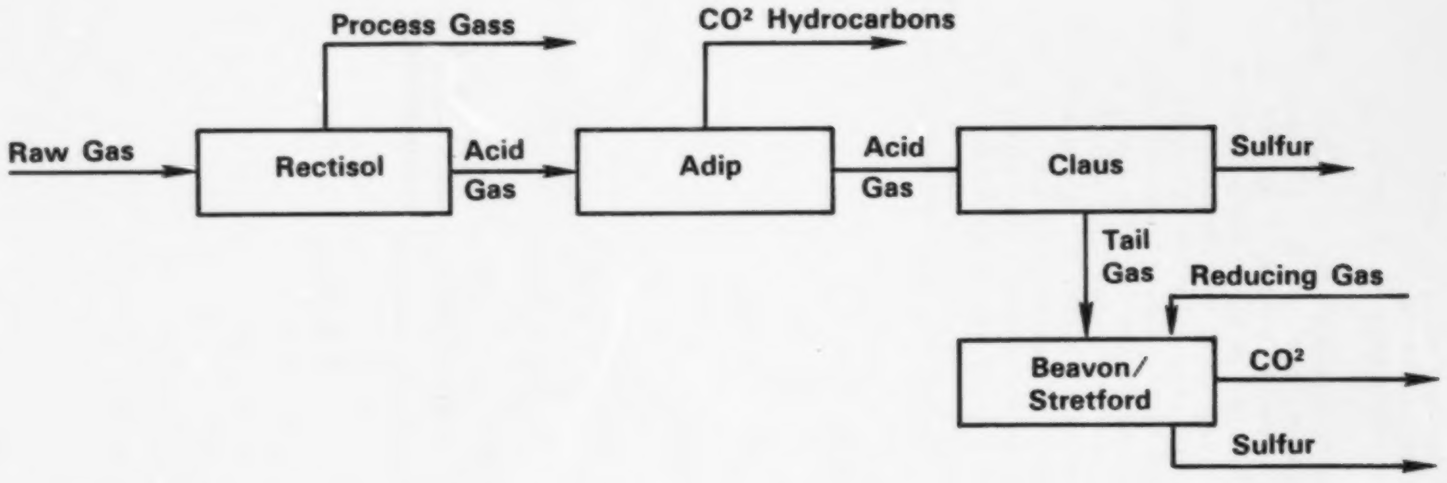
Process Gass
CO^2 Hydrocarbons
Raw Gas
Rectisol
Acid
Gas
Adip
Acid
Gas
Claus
Sulfur
Tail
Gas
Reducing Gas
Beavon/
Stretford
CO^2
Sulfur

Figure 6. Raw Gas Treating Alternate II

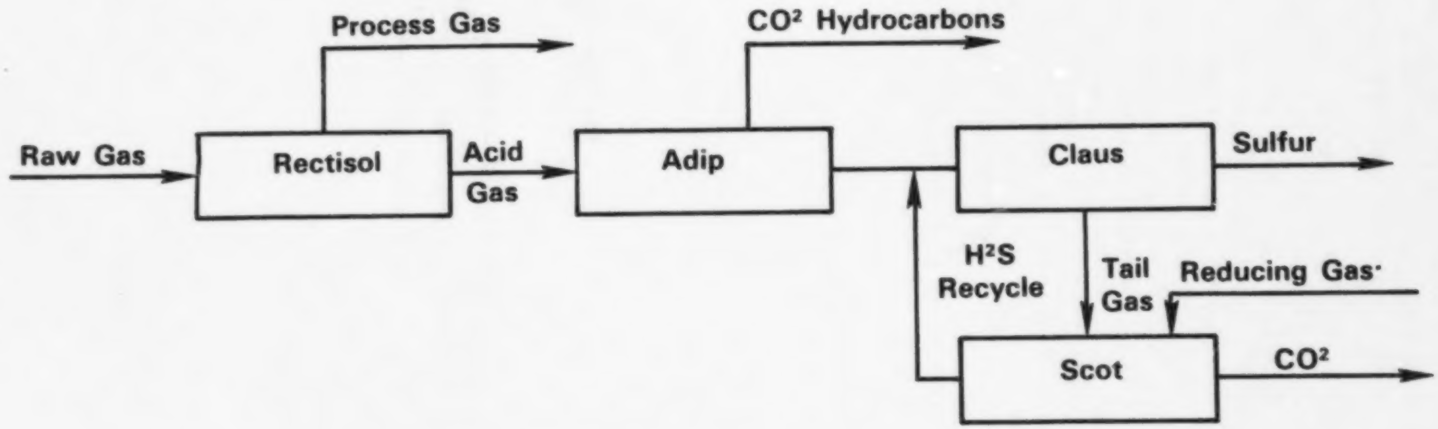
Process Gas
CO^2 Hydrocarbons
Raw Gas
Rectisol
Acid
Gas
Adip
Claus
Sulfur
H^{2}S
Recycle
Tail
Gas
Reducing Gas·
Scot
CO^2

Figure 7. Raw Gas Treating Alternate III

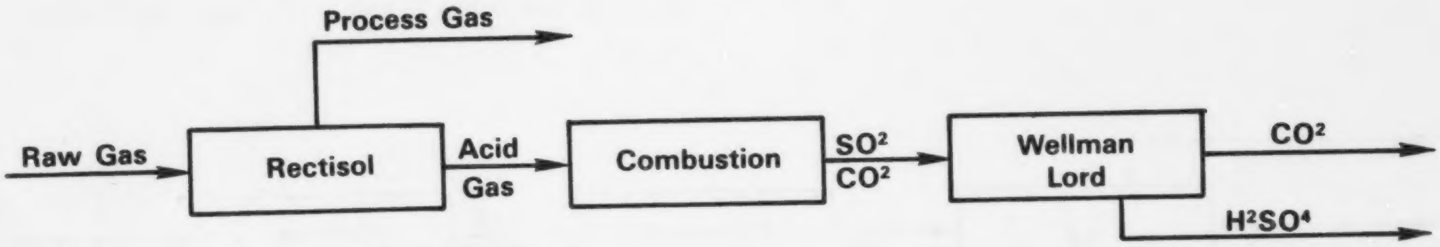
Process Gas
Raw Gas
Rectisol
Acid Gas
Combustion
SO^2
CO^2
Wellman Lord
CO^2
H^{2}SO^4

Figure 8. Raw Gas Treating Alternate IV

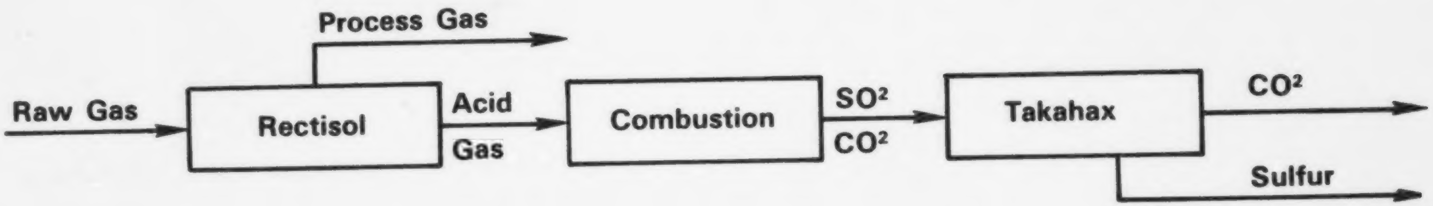
Process Gas
Raw Gas
Rectisol
Acid Gas
Combustion
SO^2
CO^2
Takahax
CO^2
Sulfur

Figure 9. Raw Gas Treating Alternate V

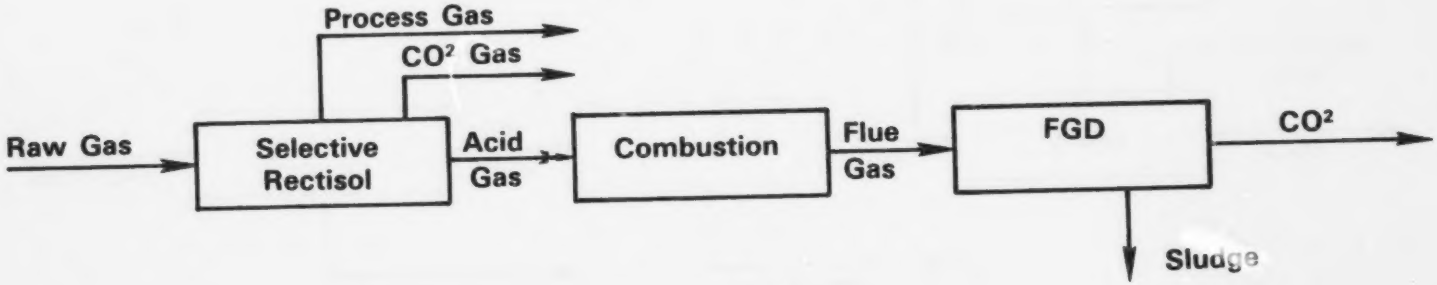
Process Gas
CO^2 Gas
Raw Gas
Selective Rectisol
Acid Gas
Combustion
Flue Gas
FGD
CO^2
Sludge

Figure 10. Raw Gas Treating Alternate VI

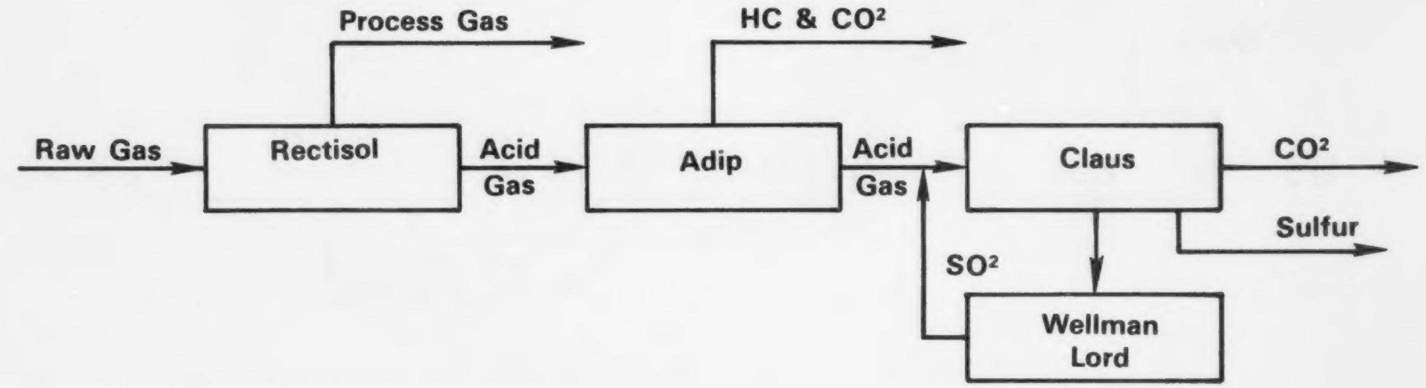
Process Gas
HC & CO^2
Raw Gas
Rectisol
Acid Gas
Adip
Acid Gas
Claus
CO^2
Sulfur
SO^2
Wellman Lord

Figure 11. Raw Gas Treating Alternate VII

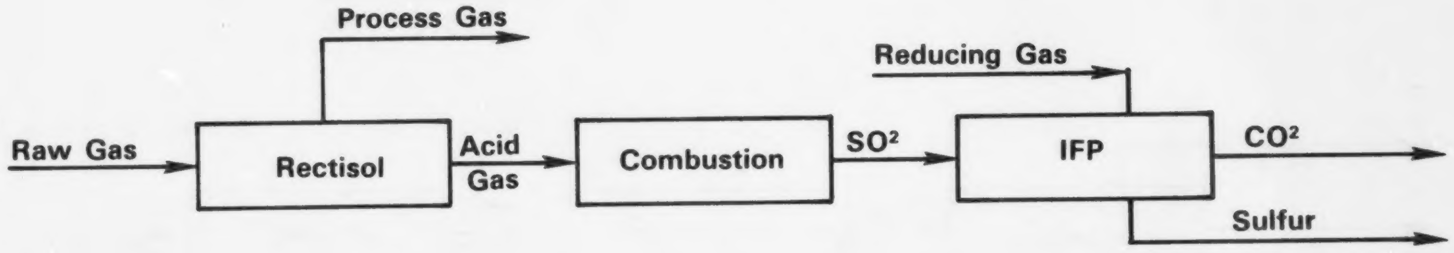
Process Gas
Reducing Gas
Raw Gas
Rectisol
Acid Gas
Combustion
SO^2
IFP
CO^2
Sulfur

Figure 12. Raw Gas Treating Alternate VIII

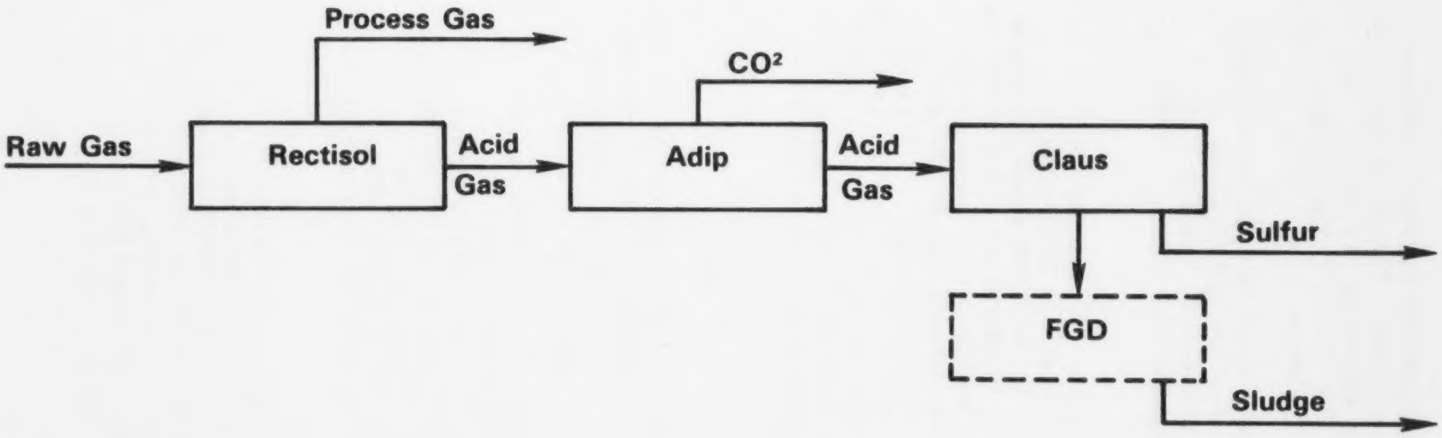
Raw Gas
Rectisol
Process Gas
Acid Gas
Adip
CO^2
Acid Gas
Claus
Sulfur
FGD
Sludge

Figure 13. Raw Gas Treating Alternate IX

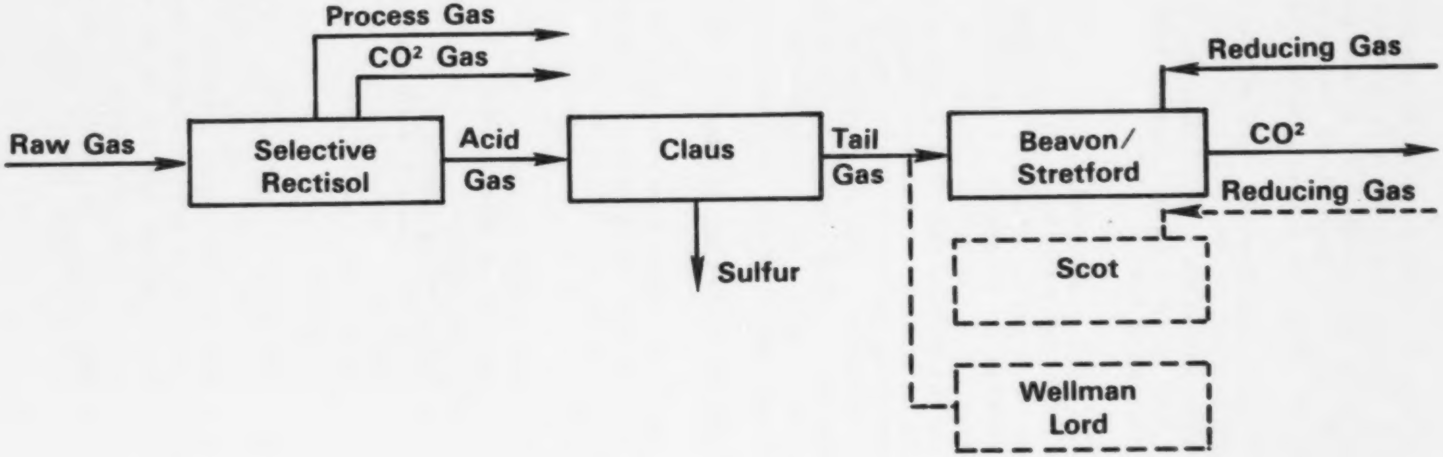
Raw Gas
Selective Rectisol
Process Gas
CO^2 Gas
Acid Gas
Claus
Sulfur
Tail Gas
Beavon/ Stretford
Reducing Gas
CO^2
Reducing Gas
Scot
Wellman Lord

Figure 14. Raw Gas Treating Alternate X

Some prescreening must be done before designs and estimates proceed to perform BACT analysis in a reasonable period of time. The first prescreening step is the elimination of the processing operations which will not meet the emission regulatory requirements of New Source Performance Standards (NSPS) or Prevention of Significant Deterioration (PSD).

It is under the PSD regulations that modeling of the air dispersion characteristics of the plant site are required to estimate the amount of allowable emissions. Once this estimate is determined, those process operations which will not comply with these regulations can be eliminated from consideration.

The next prescreening step is the elimination of those processing operations that have been determined unable to meet the cost-effective demands on previous studies. Following this step, the remaining processes are reviewed to determine if they have special requirements which cannot be satisfied (e.g., availability of the required solvent, difficulty in obtaining equipment, excess delivery time for custom-made equipment, etc.). Finally, a review is conducted regarding the commercial applicability of the remaining processes to determine whether they have been proven in pilot plant, semicommercial, or commercial operations. A cost estimate is made for the two or three remaining process operations resulting from the prescreening steps. The most cost-effective operation that satisfies the regulatory requirements is then selected.

BEST AVAILABLE CONTROL TECHNOLOGY (BACT)

There have been numerous studies made for the Environmental Protection Agency (EPA) and Department of Energy (DOE) to determine the best control scheme for given conditions or plant sites. A list of these studies and the selected acid gas removal and treatment schemes follows:

1. EPA 650/2-74-009-b, June 1974, "Evaluation of Pollution Control in Fossil Fuel Conversion Processes; Gasification: Section 1: Synthane Process," by Esso Research and Engineering Company. The Benfield Process was selected for acid gas removal with the Stretford Process for sulfur recovery. An economic evaluation of the scheme was not indicated. Selection is assumed to be based on engineering judgment.

2. EPA 650/2-74-009-c, July 1974, "Evaluation of Pollution Control in Fossil Fuel Conversion Processes; Gasification; Section I: Lurgi Process," by Exxon Research and Engineering. Acid gas treatment was mainly based on the Stearns-Roger design for the El Paso Natural Gas Company. Rectisol with Stretford Process was selected. The selection was apparently the result of economic studies conducted by Stearns-Roger for El Paso.

3. EPA 650/2-74-009-b, December 1974, "Evaluation of Pollution Control in Fossil Fuel Conversion Processes, Gasification; Section I: CO_2 Acceptor Process," by Exxon Research and Engineering Company. The study states "consideration should be given to using an absorption/oxidation process such as Stretford, Takahax, IFP, etc., on the raw gas directly."

4. EPA 650/2-74-009-g, May 1975, "Evaluation of Pollution Control in Fossil Fuel Conversion Process; Gasification: Section 5. BI-GAS Process," by Exxon Research and Engineering. Benfield with Claus and tail gas recovery was selected for acid gas removal. This study did not include an economic evaluation. Selection was assumed to be based on engineering judgment.

5. EPA 650/2-74-009-j, September 1975, "Evaluation of Pollution Control in Fossil Fuel Conversion Processes; Gasification: Section 8. Winkler Process," by Exxon Research and Engineering Company. Benfield utilizing the selective mode of operation for acid gas removal was employed. A Claus Sulfur Plant with a Tail Gas Unit was selected for sulfur removal from acid gas. No economic evaluation was indicated.

6. EPA 650/2-74-072, July 1974, "Sasol-Type Process for Gasoline Methanol, SNG, and Low-Btu Gas from Coal," by M. W. Kellogg Co. Nonselective Rectisol plus Stretford Processes for removal of acid gas were utilized. No economic evaluation was indicated. Selection was assumed to be based on engineering judgment.

7. EPA 600/2-76-101, April 1976, "Evaluation of Pollution Control in Fossil Fuel Conversion Processes: Final Report," by Exxon Research and Engineering Company. For acid gas removal units, the study states: "Each case must be examined individually, not only to choose the best type of acid gas removal process for the particular application, but also as to what modification to choose for the best type."

8. EPA-450/2-78-012, March 1978, "Guideline Series Control of Emissions from Lurgi Coal Gasification Plants," by the Environmental Protection Agency. The cost study compared: (1) Selective Rectisol, Stretford Unit on lean H_2S stream, Claus Plant followed by Tail Gas Incinerator on H_2S-rich stream, (2) Nonselective Rectisol, Stretford Unit and Tail Gas Incinerator, and (3) Selective Rectisol, Stretford Unit and Tail Gas Incinerator on lean gas stream, Claus Plant with Tail Gas Incinerator and tail gas scrubbing on H_2S-rich gas stream. A cost analysis indicated that the Nonselective Rectisol Process with a Stretford Unit was the most acceptable alternative from cost standpoint with comparable sulfur recovery efficiency.

9. DOE No. FE-2240-50, August 1978, "Sulfur Recovery in a Coal Gasification Plant," by C. F. Braun. Five different processing schemes were evaluated for both western and eastern coals. The study indicated that the Nonselective Selexol with Stretford Process and FMC Double-Alkali for boiler gas treating were the best selections for western (low-sulfur) coal. Selective Selexol with the Claus Plant and FMC Double-Alkali for the Boiler and tail gas treating were found most favorable for eastern coal. This study had one significant qualification: "Due to the large number of available alternatives and the limited number of cases that have been considered, the conclusions are only tentative."

10. DOE PNL 3140, September 1979, "Assessment of Environmental Control Technologies for Koppers-Totzek, Winkler and Texaco Coal Gasification Systems," by Pacific Northwest Laboratory. Acid gas removal discussions were general in nature.

11. ORNL-5722, August 1981, "The Impact of Environmental Control Costs on an Indirect Coal Liquefaction Process," by Oak Ridge National Laboratory/Fluor E & C, Inc., Houston, Texas. Six different cases were evaluated based on different stringency control and plant sizes. Case 4 contained the most stringent controls and an evaluation of methods of Boiler Flue Gas Emission Control. Nonselective Rectisol with a Flue Gas Desulfurization Unit was selected for the less stringent cases. Nonselective Rectisol with the Stretford Process was utilized for the most stringent control.

The various studies discussed indicate that selection of the most favorable process for acid gas removal and control of sulfur emissions is dependent upon the gasification process selected and the site location.

Coal gasification plants that utilize a coal-fired boiler for steam and power production may find it advantageous to integrate the boiler plant flue gas treating with the acid gas treating. This integration provides additional alternate schemes for consideration. Sulfur concentrations in boiler plant flue gases are low when compared to sulfur concentrations in the raw gas and acid gas streams. A sulfur removal efficiency of greater than 90 percent from boiler flue gases on a continuous basis places an excessive burden on the state of the art for some of the FGD processes. Table 3 illustrates the difference in sulfur concentrations of flue gas and Lurgi acid gas streams when processing Illinois No. 6 coal. Efficiency of removal is dependent on inlet flue gas concentration. This factor must be considered when integrating the acid gas treating system. In some instances, the acid gas stream routed to the FGD Unit may not have sufficient concentration to justify FGD treatment.

TABLE 3. ILLINOIS NO. 6 COAL - SULFUR CONTENT COMPARISON
(CALCULATED FROM ESTIMATED YIELD DATA)

	Lurgi Raw Gas	Acid Gas	Boiler Flue Gas
Gas Volume %	1% as H_2S	3.23% as H_2S	0.21% as SO_2

The cost of gas produced in a coal gasification plant is not competitive with the current cost of natural gas. Nonjustifiable expenditures resulting from delays in obtaining permits and from unnecessary environmental control systems create even more of a negative cost impact. Since synfuels plants are experiencing difficulty in meeting return on investment requirements essential for financing, every effort must be made to eliminate expenditures caused by unnecessary regulatory requirements.

BACT determinations and PSD regulations often create delays which outweigh their benefits. The regulations are burdening for both the regulator and those being regulated. Arriving at an agreement on a BACT determination, containing numerous options, creates never-ending arguments. On a case-by-case basis, these arguments become extremely burdensome for both the regulatory agency and the permittee. Allocation of PSD increments to satisfy all permittees is an assignment given to our regulators even though it is doubtful that Solomon, the wise man, could find a satisfactory solution to this problem.

Suggestions for better solutions to environmental regulations are as numerous as the process operations available for acid gas removal and treatment. Unfortunately, each solution is usually self-serving for those proposing the suggestion and does not consider the adverse effects on others. It is extremely difficult to arrive at a solution that is beneficial to the majority, since an active minority is often a controlling element in our political arena.

Industry, regulators and environmentalists must cease their role as adversaries and become partners in establishing regulations that provide maximum benefit to the majority. Since very few people can say their interests lie entirely in one direction, it should not be so difficult to work together for such a worthy goal.

Session IV: SOLID WASTE-RELATED ENVIRONMENTAL CONSIDERATIONS

Chairman: David A. Kirchgessner
U.S. Environmental Protection Agency
Research Triangle Park, NC

Cochairman: Kimm W. Crawford
TRW, Inc.
Redondo Beach, CA

PB83-128371

HEALTH EFFECTS BIOASSAY RESULTS FROM COAL CONVERSION SOLID WASTES*

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Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

ABSTRACT

To assist EPA and DOE in identifying solid wastes that may pose a potential hazard to human health and environment, the Oak Ridge National Laboratory has conducted studies on extracts from solid wastes obtained from various coal liquefaction and gasification processes. Analytical procedures to chemically characterize and separate the organic and inorganic constituents were developed. Various approaches to extraction were compared. Batteries of health effects and environmental assays were applied to the extracts or fractions thereof to serve as indicators of chronic hazards. The applicability and compatibility of the coupled chemical and biological procedures will be evaluated with particular emphasis on the Ames mutagenicity test.

INTRODUCTION

Recent examples of improper disposal at various hazardous chemical sites has dramatically increased the public awareness of the environmental and health effects associated with the disposal of solid and hazardous wastes (1). Therefore, increased emphasis has recently been placed on the regulatory aspects of the transport, treatment, storage and disposal of solid industrial waste (2).

At the same time, trends toward increased use of coal reserves in this country dictates that large volumes of solid wastes will result from various coal conversion technologies (3,4). These wastes include solids from coal-cleaning processes, flue-gas disulfurization sludges from ancillary boilers, spent catalysts, tar and oil sludges, and ash/slags. While the ashes and slags will constitute the largest volume of waste generated (> 90%), they are by and large devoid of organic material (5,6). Also, the sorptive capacity of these materials is usually large (6), and organic matter is not likely to migrate in the environment by dissolution. Thus, the environmeal and health consequences of these materials can largely be predicted from studies of inorganic content and leachability.

In the case of wastewater treatment plant sludges, which will be generated in considerably smaller but still signficant volumes, the organic content is likely to be much higher (7), and the leachability of organics from these solid wastes must be studied with respect to health and environmental effects.

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*Research sponsored jointly by the U.S. Environmental Protection Agency (IAG 78-DX-0372) and the Office of Health and Environmental Research, U. S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

This is not to imply that inroganics should be ignored in such wastes, but only to indicate the presence of a new set of risks.

The steps involved in evaluating the health and environmental effects of wastewater treatment plant sludges from coal conversion solid wastes include: 1) physical/chemical characterization of the specific wastes; 2) determination of the environmental mobility of the various chemical constituents of the waste by evaluation of aqueous extracts intended to simulate specific disposal scenarios, and 3) preparation of the wastes and aqueous extracts for bioassay. This work represents a summary of data relevant to these three areas.

MATERIALS AND METHODS

Sample Collection

Samples were collected from operating pilot plants during a steady-state period Sample 1 was a filtered sludge from a pilot-scale coal liquefaction wastewater treatment plant, Sample 2 was collected from a coal cleaning plant and represented the final wastewater treatment plant solid waste. Sample 3 was collected as a centrifuged-residual from a liquefaction wastewater treatment plant.

Generation of Aqueous Extracts of Solid Wastes

Five techniques were used for the generation of aqueous extracts of the solid wastes. These included the EPA-EP, a distilled water extraction carried out in a manner identical to the EPA-EP (H_2O-EP), a sodium-resin displacement extraction, a citric acid extraction and an upward-flow column extraction with distilled water. The EPA-EP and the citric acid extractions are intended to mimic the co-disposal of municipal and industrial solid waste. The distilled water EP and sodium displacement techniques are more applicable to the disposal scenario of 100% industrial waste. The upward flow column extraction can be used to simulate either scenario depending on the extractant, but is primarily intended to avoid the artificial solid/solution separations inherent in the batch extractions, regardless of the extractant used. The variable and constant factors involved in the extractions are listed in Table 1.

Preparation of Solid Wastes and Extracts from Ames Bioassay

The solid wastes were prepared for the Ames test (8) in two ways. The solid wastes (50 g) were Soxhlet-extracted for 24 hours using methylene chloride (9). An aliquot of the Soxhlet extract was concentrated to dryness and redissolved in 2 ml dimethylsulfoxide. This solution was bioassayed.

In addition, the solid wastes were extracted using a three-step extraction procedure (10). Briefly, this procedure involves equilibration of the solid waste with acid, followed by base, followed finally by organic solvent. Thus, the procedure results in three fractions for bioassay: acids, bases

TABLE 1

EXTRACTION PROCEDURES: IDENTIFICATION OF VARIABLE AND CONSTANT LEACHING FACTORS

	Variable Factors			
Extraction	Initial Leaching Medium	Mode of Extraction	pH Adjustment	Treatment of Leachate Solution for Extract Analysis
1. EP	Distilled deionized	Batch: magnetically stirred	Adjust to pH 5 with 0.5 N acetic acid - maximum limit of 2 meq/g sample	Pressure filtered through 0.4 μm nuclepore filter
2. Water	Distilled deionized water	Batch: magnetically stirred	None	Pressure filtered through 0.4 μm nuclepore filter
3. Na-Resin	Distilled deionized water with 1 g calculated dry wt chelex 100/10 g sample	Batch: magnetically stirred	Adjust to pH 7 with 0.1 N HCl	Pressure filtered through 0.4 μm nuclepore filter
4. Citrate Buffer	0.5 M citrate buffer	Batch: rotary extractor	None	Pressure filtered through 0.4 μm nuclepore filter
5. Column	Distilled deionized water	Column: upward flow	None	Leachate from column directly passed through XAD-2 resin

Constant Factors

Factor	Condition Used
1. Sample particle size	< 9.5 mm
2. Extraction temperature	room temperature
3. Extraction time:	
Batch mode	24-hour
Column	until effective solid:solution ratio is reached
4. Number of leachings on same sample	1
5. Effective solid:solution ratio	1:20

and neutrals. An aliquot of easch fraction was concentrated to dryness and redissolved in dimethylsulfoxide for the Ames test.

The aqueous extracts were prepared as follows: a 500 ml aliquot was adjusted to pH 6.8 using phosphate buffer and to conductivity 20 mS using sodium chloride. The adjusted extract was passed through a column containing 4 ml XAD-2 resin. The resin was eluted with 20 ml acetone. The acetone was concentrated to dryness and the residue taken up in 2 ml dimethylsulfoxide. In the case of the column extraction, the XAD-2 was located directly above the column. This XAD-2 was extracted in a manner identical to that used in the batch extractions. An aliquot of the acetone was evaporated to dryness and taken up in 2 ml dimethylsulfoxide.

Analysis of Wastes and Extracts

All extract and fractions described above were characterized using gas chromatography and combined gas chromatography/mass spectrometry. GC was done on a Hewlett-Packard Model 5736-A gas chromatograph equipped with a flame ionization detector and a H-P Model 3390 integrator. A twenty-five meter fused silica capillary column (J&W Scientific) was used. GC/MS was done on a H-P Model 5985-A GC/MS/DS equipped with a similar column.

When possible, the solid waste extracts were applied to a preweighed filter pad; the solvent was evaporated and the pad reweighed. The difference was used as a crude indication of the mass of material present.

Ames Mutagenicity Test

The general methodology for the Salmonella/microsome assay has been described (11). In screening mode, the assay is restricted to two strains: TA 100, the hisG base-pair substitution in the uvrB rfa pKM101 background and TA 98, the hisD frameshift, also carrying uvrB rfa and pKM101. The full range of metabolic activation was examined, however, using microsomal preparations from both phenobarbital and Arochlor-treated rats.

RESULTS AND DISCUSSION

Analysis of Solid Wastes and Extracts

The results of the characterization work on the solid wastes and extracts are reported elsewhere (7), however, some general comments are appropriate here. In terms of the wastes themselves, considerably more organic material was extracted using the three-step procedure than was extracted by the Soxhlet extraction. This is true in terms of total mass as well as in terms of the levels of individual compounds. Qualitatively, the three wastes were similar. All contained a variety of compounds, although the neutral fraction was responsible for much of the organic content. All contained aromatic hydrocarbons and aromatic heterocycles (including nitrogen, oxygen, and sulfur containing species). In addition, all contained significant quantities of volatile organic compounds. Therefore, any assessment of the health and environmental effects of these materials must consider potential inhalation and air-quality problems. The levels of organics were highest from Sample 3 followed by Sample 1, and finally Sample 2.

The characterization of the aqueous extracts revealed the following general trends. The levels of organic materials in the extracts were more closely related to the technique used for extraction than to the extraction medium. For example, the extraction of volatile organics appeared to be superior in the citrate buffer extraction. However, this extraction is carried out in a closed system. Use of distilled water in the closed extractor produced comparable levels of volatile organics. Conversely, the extraction of phenol and the cresols did not appear to be relatd to the pH of the extractant. While no one batch extraction procedure was consistently superior in terms of extracting organics, when the organic content of the solid waste was high (e.g., Sample 3) all procedures were comparable. When the organic content of the solid wastes was low, the distilled water-EP appeared to be the most effective batch extraction technique.

The column extraction consistently extracted higher levels of organic compounds than did any of the batch extractions. This is due partly to the fact that no filtration is required, but also partly due to more aggressive displacement of organic compounds. This is particularly true when considering nonpolar compounds.

Ames Bioassay Results

The Ames Salmonella mutagenesis bioassay is widely recognized as an indicator of bacterial mutagenesis. It may also be an indicator of potential mammalian carcinogenesis. The test has the advantages of being relatively inexpensive, short-term, and simple to perform. The test is primarily sensitive to organic mutagens; thus, the characterization work described earlier is directly applicable to the Ames test.

The bioasay results from Samples 1 and 2 are shown in Tables 2 and 3. The extracts of Sample 1 were all extremely toxic. There was an indication of mutagenic activity in all but the most toxic extracts. The most active extract was the acid fraction, showing a non-linear dose-response in TA 98 (with phenobarbital activation) giving a peak mutation induction 15-fold over the untreated control (Figure 1). The extracts of Sample 2 were non-mutagenic, and only the Soxhlet extract and the acid fraction showed significant non-specific toxicity. The extracts of Sample 3 were extremely toxic; even at a 10-fold dilution these samples were too toxic for assay.

The results of the Ames test on the aqueous extracts of Sample 1 are shown in Table 4. Again, all exhibited some degree of toxicity. Those extracts which were not too toxic to test displayed mutagenic activity. The aqueous extracts of Sample 2 were not active in either strain. Extracts from Sample 3 were diluted 10-fold and the results are shown in Table 5. All were mutagenic including the EP extract, which displayed a linear dose-response (Figure 2), even after dilution.

TABLE 2
MUTAGENICITY OF SOLID WASTE SAMPLE 1

Revertants/plate

	TA 98				TA 100			
Conc (μl/plate)	Soxhlet	Acid	Base	Neutral	Soxhlet	Acid	Base	Neutral
PHENOBARBITAL ACTIVATION								
75	T*	T	T	T	T	T	T	T
50	93	609	T	60	T	670	T	T
25	94	556	T	61	T	645	T	T
10	97	391	T	52	T	536	T	T
0	22	39	22	42	199	167	91	106
AROCHLOR ACTIVATION								
75	T	T	T	T	T	T	T	T
50	T	T	T	T	T	T	T	T
25	70	156	T	I	T	T	T	T
10	70	202	T	54	T	229	T	T
0	22	48	42	35	192	126	153	123
NO ACTIVATION								
50	T	T	T	T	150	T	T	T
0	21	40	27	44	105	159	153	99

TABLE 3
MUTAGENICITY OF SOLID WASTE SAMPLE 2

Revertants/plate

	TA 98				TA 100				
Conc (µl/plate)	Soxhlet	Acid	Base	Neutral	Soxhlet		Acid	Base	Neutral
PHENOBARBITAL ACTIVATION									
75	41	65	T	57	T	T		187	162
50	33	58	53	43	T	T		187	165
25	41	60	41	35	117	227		150	163
10	47	52	71	32	112	220		216	135
0	17	47	47	19	104	173		173	174
AROCHLOR ACTIVATION									
75	T	T	46	54	T		T	207	173
50	T	T	52	40	T		T	160	160
25	T	T	46	30	T		T	138	151
10	47	39	59	32	107		231	205	163
0	27	28	28	20	98		182	182	98
NO ACTIVATION									
50	T	T	26	33	T		T	204	92
0	29	35	35	28	118		192	192	103

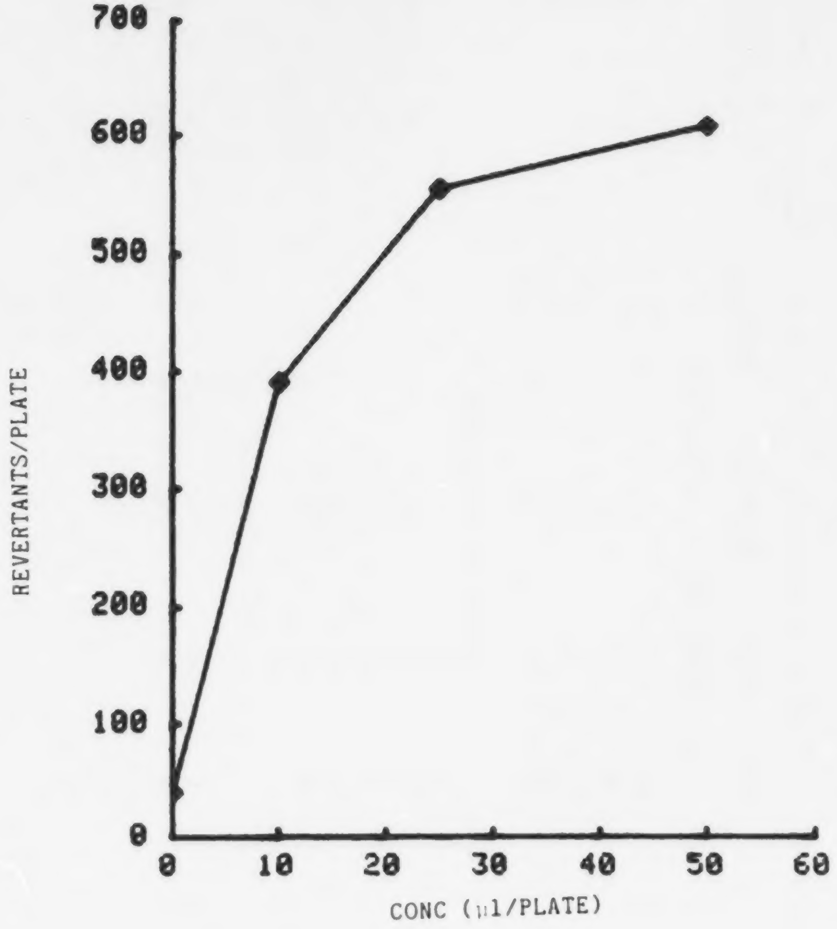

Figure 1. Mutagenicity of Acid Fraction of Sample 1
(TA 98, Phenobarbital Activation)

TABLE 4

MUTAGENICITY OF SOLID WASTE EXTRACTS FROM SAMPLE 1

Revertants/plate

	TA 98					TA 100				
Conc (µl/plate)	EP	H_2O-EP	Citrate	Na-Resin	Column	EP	H_2O-EP	Citrate	Na-Resin	Column
PHENOBARBITAL ACTIVATION										
75	T	T	T	T	T	T	T	T	T	T
50	T	T	T	T	T	T	T	T	T	T
25	T	58	T	35	94	T	T	T	T	T
10	44	41	45	33	78	156	T	T	117	149
0	17	52	22	16	42	109	110	154	111	112
AROCHLOR ACTIVATION										
75	T	T	T	T	T	T	T	T	T	T
50	T	T	T	T	T	T	T	T	T	T
25	T	T	T	T	119	T	T	T	T	T
10	31	42	T	19	48	T	T	T	108	117
0	13	43	28	8	31	96	91	167	94	108
NO ACTIVATION										
50	T	T	T	T	T	T	109	T	T	T
0	7	42	58	17	42	94	76	110	71	111

TABLE 5
MUTAGENICITY OF BATCH EXTRACTS FROM SAMPLE 3

Revertants/plate

	TA 98				TA 100			
Conc (μl/plate)	EP	H_2O-EP	Citrate	Na-Resin	EP	H_2O-EP	Citrate	Na-Resin
				PHENOBARBITAL ACTIVATION				
7.5	110	34	71	T	T	T	163	119
5.0	92	52	57	45	T	71	213	165
2.5	46	45	54	46	117	136	169	125
1.0	30	27	49	70	93	119	152	123
0	19	16	42	22	85	80	150	106
				AROCHLOR ACTIVATION				
7.5	98	74	80	T	T	T	156	151
5.0	59	52	86	T	T	T	165	109
2.5	53	27	48	110	T	78	214	182
1.0	29	29	39	97	78	70	176	143
0	20	18	40	29	65	74	135	110
				NO ACTIVATION				
5.0	7	9	42	27	T	T	95	120
0	4	7	30	22	40	30	95	85

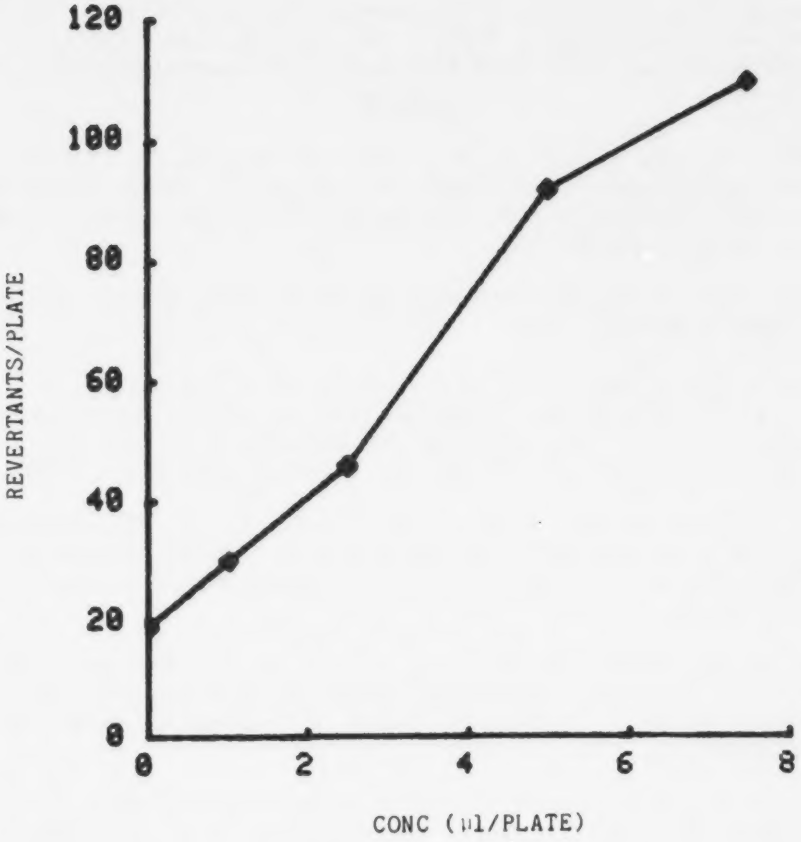

Figure 2. Mutagenicity of EP Extract of Sample 3 (TA 98, Phenobarbital Activation)

SUMMARY

The organic content of three solid wastes, representing coal conversion wastewater treatment plant sludges, were compared. State-of-the-art analytical techniques coupled with the Ames mutagenesis bioassay were used. A three-step fractionation/isolation scheme improved the bioassay results by isolating toxicity in the "acid" fraction. In addition, the wastes were extracted using five different environmental mobility tests. The extracts were analyzed and assayed (Ames test). In general, the results of the Ames Bioassay parallelled the results of the analytical characterization.

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A COMPARISON OF RCRA LEACHATES OF SOLID WASTES FROM COAL-FIRED UTILITIES † AND LOW- AND MEDIUM-BTU GASIFICATION PROCESSES

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ABSTRACT

EPA has promulgated regulations which temporarily exclude utility wastes, including fly ash and bottom ash from coal-fired generating stations, from Subtitle C of Resource Conservation and Recovery Act (RCRA) regulations. EPA, using broad interpretation of amendments to the act, has also excluded coal gasification solid wastes from Subtitle C regulations and these wastes are listed as non-hazardous pending further data evaluation. This paper presents comparative results of RCRA leachates of the solid wastes from two low-BTU gasification processes and coal-fired utility solid wastes. The three facilities from which solid wastes were obtained used the same lignite feedstock. Also presented are comparable RCRA leachate results of solid wastes from a medium-BTU gasification process and a coal-fired power plant, both fueled with identical lignite feedstocks. The results indicate that solid wastes from coal-fired utilities and the solid wastes generated directly by low- and medium-BTU gasification processes are non-hazardous according to RCRA protocol and limits.

INTRODUCTION

On May 19, 1980, EPA promulgated regulations implementing Subtitle C of the Resource Conservation and Recovery Act (RCRA). The regulations define solid and hazardous wastes and establish criteria for handling and disposal of hazardous wastes. Excluded from Subtitle C regulations were fossil fuel combustion wastes which were then the subject of pending Congressional legislation. The Solid Waste Disposal Act of October 21, 1980 mandated the exclusion of fossil fuel combustion wastes from Subtitle C regulations and includes specifically fly ash waste and bottom ash waste of coal combustion processes (Reference 1).

The exclusion of coal combustion solid wastes from Subtitle C regulations is temporary. A revision of the exclusion of these wastes may be enacted pending the assessment of the environmental effect of these wastes by EPA.

Excluded from Subtitle C regulations by amendments to RCRA in November, 1980 were "solid waste from the extraction, beneficiation, and processing of ores and minerals". Under the interpretation that coal is a "mineral or ore", EPA has excluded solid wastes generated directly by coal gasification processes from Subtitle C regulations by considering gasification to be "extraction, beneficiation, and processing" of the "mineral or ore" i.e., coal. The exclusion from Subtitle C regulations of gasification solid wastes applies only to solid wastes produced directly by the gasification process. Wastes generated refining or upgrading the product are not excluded. This broad interpretation of the ruling will remain in effect until EPA has had an opportunity to evaluate the scope of specific exclusions (Reference 2).

Although the exclusion from Subtitle C regulations is temporary for both coal-fired power plants and coal gasification solid wastes, coal gasification is a fledgling industry in this nation, with limited data available to assess the environmental implications of the disposal of solid wastes generated by the various processes. On the other hand, utilities produce a substantial portion of the nation's electricity at coal-fired power plants. The characteristics of coal-fired power plant solid wastes are much more defined and recognized.

This paper presents data which provide an opportunity to evaluate comparative results of RCRA leachates of solid wastes from fossil fuel combustion and solid wastes from coal gasification processes. The data includes RCRA leachate results of the solid wastes from two low-BTU gasification processes and the solid wastes from a coal-fired power plant, the feedstocks of the three processes from the same mine. Other data presented are RCRA leachate results of a medium-BTU gasification solid waste and solid wastes from a coal-fired power plant, both facilities having the same lignite feedstock, but not the same as the low-BTU gasification feedstocks.

RCRA leachate results on the solid wastes from coal-fired power plants and gasification processes provide data developed from solid wastes produced under similar conditions. Coal-fired power plant bottom ash and coal gasification gasifier ash are subjected to the very hot temperatures associated with each process and are primarily fused ash having a coarse texture. One of the major differences of the two processes is that solid wastes from coal-fired power plants are generated in an oxidizing atmosphere while solid wastes from gasification processes are generated in a reducing atmosphere. Gasifier ash passes through both reducing and oxidizing zones within the gasifier. Wet samples of bottom and gasifier ashes are generally collected, either after sluicing to disposal ponds (bottom ash) or through the water pressure seal of the gasifier (gasifier ash). Precipitator ash and cyclone dust are finer particulate matter entrained in the combustion effluents or product gas. Precipitator ash is collected dry, but may be sluiced to disposal ponds. Cyclone dust samples are most often retrieved dry, but may be collected wet from water quench systems. The solid wastes from gasification processes (gasifier ash and cyclone dust) have considerable concentrations (approximately 20-50%) of carbon, while coal-fired power plant solid wastes have quite low concentrations (< 1%) of carbon.

TECHNICAL APPROACH

As required by RCRA, EPA has established five categories to define the characteristics of hazardous waste. The five characteristics are:

- General - a solid waste is a hazardous waste if it exhibits any of the characteristics of hazardous waste.
- Ignitability - ignitable wastes have a low flash point, or are liable to cause fires or are oxidizers.
- Corrosivity - corrosive wastes have a pH of less than or equal to 2 or greater than or equal to 12 or corrode steel at a specified rate.
- Reactivity - reactive wastes react violently, generate toxic fumes or are explosive.
- Extraction Procedure (EP) Toxicity - an extraction procedure is specified and maximum concentrations of contaminants listed; the waste is hazardous if the concentration of any contaminant in the leachate is equal to or greater than the listed contaminant level.

The extraction procedure has been designed to identify wastes which would leach hazardous concentrations of toxic constituents into groundwaters under conditions of improper management. The characteristic of EP toxicity contaminants are presented in Tables 1, 5, and 7 along with the maximum allowable concentrations of each. The list of contaminants includes eight elements, four pesticides, and two herbicides.

The conclusions presented in this paper are based upon the characteristic of EP toxicity and primarily upon the inorganic element contaminants. The contaminants listed in the EP toxicity characteristic are the toxic contaminants listed in the National Interim Primary Drinking Water Standards (NIPDWS). The maximum concentration levels of the EP toxicity contaminants are ten times the concentrations specified in the NIPDWS.

Radian Corporation is presently under contract to the EPA to conduct an "Environmental Assessment of Low/Medium-BTU Gasification Technology". As part of this program, Radian has conducted source test and evaluations at commercial and pilot scale low- and medium-BTU gasification facilities. Included in the source test and evaluations, solid wastes of the gasification processes (gasifier ash and cyclone dust) have been subjected to the RCRA extraction procedure with subsequent analyses of the leachates for the eight RCRA elemental contaminants.

Two low-BTU gasification facilities tested were a Wellman-Galusha gasifier located at the U.S. Bureau of Mines, Twin Cities Metallurgy Research Center, Ft. Snelling site, in Minneapolis, Minnesota, and the Riley Gas Producer located at the Riley Research Center in Worcestor, Massachusetts. During testing, both units were operating with North Dakota Indianhead lignite. Both gasifiers are air-blown, atmospheric pressure units. The major difference between the two gasifiers is that the Wellman-Galusha is a thick fixed-bed (app. 4 feet) design while the Riley Gas Producer is a thin fixed-bed (app. 2 feet) design. At the Ft. Snelling site (Wellman-Galusha), the cyclone dust is water quenched after removal from the product gas.

To evaluate RCRA results of coal gasification and coal-fired power plant solid wastes generated from facilities operating with the same feedstock, Radian, with the aid of American Natural Service Company, identified a coal-fired power plant using the Indianhead lignite as the feedstock. United Power association, headquartered in Elk River, Minnesota, operates a mine-mouth power plant firing Indianhead lignite in Stanton, North Dakota. Radian received samples of lignite, bottom ash, and electrostatic precipitator ash from the Stanton Plant. As with the solid wastes of the gasification processes, the coal-fired power plant solid wastes (bottom ash and precipitator ash) were subjected to the RCRA extraction procedure and the leachates analyzed for the eight RCRA elemental contaminants.

Also as part of the EPA program, Radian has conducted source test and evaluations at a commercial Lurgi-based coal gasification facility located in the Kosovo region of Yugoslavia. A coal-fired power plant also operates at the plant site and utilizes the same coal feedstock as the gasification facility. During the site testing, samples of the gasifier ash from the Lurgi gasifiers and bottom ash and precipitator ash from the power plant were collected. The three samples were subjected to the RCRA extraction procedure and the leachates analyzed for the eight RCRA elemental contaminants.

To allow an evaluation of the similarities or dissimilarities of the feedstocks of the two low-BTU gasification processes, the lignite collected at each facility was analyzed for proximate and ultimate parameters and the eight RCRA element contaminants. The solid wastes from these processes were analyzed for the eight RCRA element contaminants to assess the relationship between RCRA leachate concentrations of the RCRA element contaminants to the concentrations of these elements in the solid. Proximate and ultimate analyses were performed on the solid wastes from the two low-BTU gasification processes and the Stanton Plant to review the similarities of the solid wastes with respect to major components.

RESULTS

LOW-BTU GASIFICATION

As discussed earlier, Radian has performed source test and evaluations at several low-BTU coal gasification facilities. The results of two facilities presented in this paper have been taken from source test and evaluation programs performed at the two facilities (Reference 3 and 4). The Riley Gas Producer STER will be finalized in November of this year. The United Power Association power plant data and the medium-BTU gasification data have been generated independently of the above two projects, but have been funded by EPA.

Table 1 presents the RCRA leachate results for the eight RCRA elemental contaminants of the solid wastes from the two low-BTU gasification processes and the Indianhead lignite-fired power plant. Also presented are maximum levels of the eight contaminant elements, any of which exceeded in the RCRA leachate of the solid wastes characterize the solid waste as hazardous and regulated under Subtitle C.

The concentrations of the eight RCRA elemental contaminants of the solid wastes from the two low-BTU gasification facilities and from the coal-fired power plant are presented in Table 2.

Concentrations of the eight RCRA elemental contaminants and proximate and ultimate analytical results of the lignite feedstocks from the two low-BTU gasification facilities and the coal-fired power plant are presented in Table 3.

Presented in Table 4 are proximate and ultimate analytical results of the solid wastes from the three processes with Indianhead lignite as the feedstock to allow a comparison of wastes generated by the two low-BTU gasification processes and the coal-fired power plant.

Table 5 presents the analyses of RCRA leachates of the Riley Gas Producer gasifier ash and cyclone dust for the contaminant pesticides and herbicides. These are the only RCRA leachates which were analyzed for these contaminants.

The percent of the total element of each solid waste leached by the RCRA extraction procedure from the solid wastes from the two low-BTU gasification processes and from the coal-fired power plant operating on Indianhead lignite is presented in Table 6.

MEDIUM-BTU GASIFICATION

Table 7 presents the analytical results for the eight RCRA protocol elements of the RCRA leachates of the Lurgi gasifier ash and the bottom ash and precipitator ash from a coal-fired power plant located at the plant site and using the same coal as feedstock. The RCRA elemental contaminant maximum levels are also presented.

The elemental concentrations of the eight RCRA protocol elements in the solid wastes from the gasification facility and coal-fired power plant at the Kosovo site are presented in Table 8.

Table 9 presents the percent of the total element of each solid waste leached by the RCRA extraction procedure from the solid wastes from the medium-BTU gasification process and from the coal-fired power plant at the Kosovo plant.

TABLE 1. RCRA LEACHATE RESULTS OF LOW-BTU GASIFICATION SOLID WASTES AND COAL-FIRED POWER PLANT SOLID WASTES HAVING SAME LIGNITE FEEDSTOCK

	Wellman-Galusha (Ft. Snelling)		Riley Gas Producer		United Power Assn. Stanton Plant		RCRA Contaminant Maximum Concentration* ug/L
Contaminant	Gasifier Ash ug/L	Cyclone Dust ug/L	Gasifier Ash ug/L	Cyclone Dust ug/L	Bottom Ash ug/L	Precipitator Ash ug/L	
Arsenic	19	33	33	4	8	58	5,000
Barium	1,000**	1,000**	680	390	300	920	100,000
Cadmium	<7**	NA	<0.5	<0.5	40	50	1,000
Chromium	1**	1**	<1	<1	<200	<200	5,000
Lead	7**	8**	<2	<2	300	400	5,000
Mercury	<0.6	<0.3	<0.5	<0.5	0.3	0.4	200
Selenium	14	6	6	2	<4	87	1,000
Silver	NA	NA	<0.5	<0.5	25	30	5,000

*Reference 1

**Analysis by spark source mass spectroscopy - all other analyses by atomic absorption spectroscopy

NA - not analyzed.

TABLE 2. ELEMENTAL CONCENTRATIONS OF LOW-BTU GASIFICATION SOLID WASTES AND COAL-FIRED POWER PLANT SOLID WASTES*

	Wellman-Galusha† (Ft. Snelling)		Riley Gas Producer††		United Power Assn. Stanton Plant	
Element	Gasifier Ash ug/g	Cyclone Dust ug/g	Gasifier Ash ug/g	Cyclone Dust ug/g	Bottom Ash ug/g	Precipitator Ash ug/g
Arsenic	30**	63**	58**	0.6**	19	53
Barium	1900***	630	3300***	1700***	>1000	>1000
Cadmium	0.8	2	<3	<0.1	2	2
Chromium	21***	<6.2***	<0.2***	43***	26	12
Lead	5	8	7	37	17	18
Mercury	1.7**	<3.2**	0.0005**	0.02**	NA	NA
Selenium	15**	14**	<1**	1.2**	4	10
Silver	0.6	2	<3	<0.1	<0.8	<0.4

*Analysis by spark source mass spectroscopy
**Analysis by atomic absorption spectroscopy
***Analysis by inductively coupled plasma emission spectrooscopy
NA-Not analyzed
†Reference 3
††Reference 4

TABLE 3. RCRA ELEMENTAL CONTAMINANTS AND PROXIMATE AND ULTIMATE ANALYTICAL RESULTS, INDIANHEAD LIGNITE FEEDSTOCKS*

	Wellman-Galusha† (Ft. Snelling) Lignite	Riley Gas Producer†† Lignite	United Power Assn. Stanton Plant Lignite
Proximate Analysis			
% Ash	10.91	12.09	9.15
% Volatile	41.93	42.40	39.69
% Fixed Carbon	47.16	45.51	51.16
BTU/lb	10475	10630	10923
% Sulfur	0.61	1.10	1.04
Ultimate Analysis			
% Carbon	62.69	63.32	66.27
% Hydrogen	4.60	4.31	4.41
% Nitrogen	0.91	1.02	0.75
% Chlorine	0.03	0.002	0.00
% Sulfur	0.61	1.10	1.04
% Ash	10.91	12.09	9.15
% Oxygen (diff.)	20.25	17.94	18.38
% H_2O		32.8	32.9
Arsenic	6.5***	23***	11**
Barium	630**	430****	>1000**
Cadmium	0.4**	3**	0.2**
Chromium	10**	3.2****	0.2**
Lead	2**	2**	1**
Mercury	0.4***	0.15***	NA
Selenium	1***	<0.5***	<0.1**
Silver	1**	<4**	0.1**

*dry basis

**analysis by spark source mass spectroscopy

***analysis by atomic absorption spectroscopy

****analysis by inductively coupled plasma emission spectroscopy

NA-not analyzed

†Reference 3

††Reference 4

TABLE 4. PROXIMATE AND ULTIMATE ANALYTICAL RESULTS OF LOW-BTU GASIFICATION SOLID WASTES AND COAL-FIRED POWER PLANT SOLID WASTES OPERATING ON INDIANHEAD LIGNITE*

	Wellman-Galusha** (Ft. Snelling)		Riley Gas Producer***		United Power Assn. Stanton Plant	
	Gasifier Ash	Cyclone Dust	Gasifier Ash	Cyclone Dust	Bottom Ash	Precipitator Ash
Proximate Analysis						
% Ash	74.41	18.97	62.54	39.93	98.68	99.57
% Volatile	6.56	24.41	10.59	15.00	3.92	3.98
% Fixed Carbon	19.03	56.62	26.87	45.08	-2.60	-3.65
BTU/lb	3747	10717	4993	8478	0	0
% Sulfur	1.09	1.51	1.64	1.67	0.01	0
Ultimate Analysis						
% Carbon	24.64	67.18	35.36	53.69	0.96	0.55
% Hydrogen	0.41	2.32	0.61	1.52	0.04	0.07
% Nitrogen	0.17	0.93	0.46	0.82	0.07	0.04
% Chlorine	0.02	0.03	0.003	0	0	0
% Sulfur	1.09	1.51	1.64	1.67	0.01	0
% Ash	74.41	18.97	62.54	39.93	98.68	99.67
% Oxygen (diff.)	0.60	9.06	0	2.39	0.24	-0.33

*dry basis
**Reference 3
***Reference 4

TABLE 5. RCRA PESTICIDE/HERBICIDE CONTAMINANTS RESULTS OF LOW-BTU GASIFICATION SOLID WASTES LEACHATES

	Riley Gas Producer*		RCRA
Contaminant	Gasifier Ash (ug/L)	Cyclone Dust (ug/L)	Contaminant Maximum Concentration** (ug/L)
Endrin	BDL	BDL	20
Lindane	BDL	BDL	400
Methoxychlor	BDL	BDL	10,000
Toxaphene	BDL	BDL	500
2,4-D	BDL	BDL	10,000
2,4,5-TP Silvex	BDL	BDL	1,000

BDL - Below detection limit

Detection Limits:

Endrin	<2 ug/L
Lindane	<0.2 ug/L
Methoxychlor	<2 ug/L
Toxaphene	<100 ug/L
2,4-D	<0.8 ug/L
2,4,5-TP Silvex	<0.3 ug/L

*Reference 4
**Reference 1

TABLE 6. LOW-BTU GASIFICATION AND COAL-FIRED POWER PLANT RCRA LEACHATES OF SOLID WASTES PERCENT OF TOTAL ELEMENT LEACHED

	Wellman-Galusha (Ft. Snelling)		Riley Gas Producer		United Power Assn. Stanton Plant	
Contaminant	Gasifier Ash	Cyclone Dust	Gasifier Ash	Cyclone Dust	Bottom Ash	Precipitator Ash
Arsenic	1.3	1.0	1.1	13.3	0.84	2.6
Barium	1.1	0.9	0.4	0.5	>0.6****	<1.8****
Cadmium	<17.5*	NA	***	***	40	50
Chromium	0.1	>0.3**	***	<0.05*	<33.3*	<33.3*
Lead	2.8	2.0	<0.6*	<0.1*	35.3	44.4
Mercury	<0.7*	***	<2000*	<50	NA	NA
Selenium	1.9	0.9	>12**	3.3	<2*	17.4
Silver	NA	NA	***	***	>62.5**	>150**

NA-not analyzed

*Leachate concentration below lower detection limit.

**Solid concentration below lower detection limit.

***All results below lower detection limit.

****Solid concentration above upper detection limit.

TABLE 7. RCRA LEACHATE RESULTS OF MEDIUM-BTU GASIFICATION SOLID WASTE AND COAL-FIRED POWER PLANT SOLID WASTES HAVING SAME LIGNITE FEEDSTOCK*

Contaminant	Lurgi Gasifier Ash ug/L	Power Plant Bottom Ash ug/L	Power Plant Precipitator Ash ug/L	RCRA Contaminant Maximum Concentration** ug/L
Arsenic	21	9	<3	5,000
Barium	1200	510	410	100,000
Cadmium	<0.5	<0.5	<0.5	1,000
Chromium	330	130	140	5,000
Lead	140	47	250	5,000
Mercury	<0.2	<0.2	<0.2	200
Selenium	<4	<4	<4	1,000
Silver	<1	<1	<1	5,000

*Analysis by atomic absorption spectroscopy
**Reference 1

TABLE 8. ELEMENTAL CONCENTRATIONS OF MEDIUM-BTU GASIFICATION SOLID WASTE AND COAL-FIRED POWER PLANT SOLID WASTES*

Element	Lurgi Gasifier Ash ug/g	Power Plant Bottom Ash ug/g	Power Plant Precipitator Ash ug/g
Arsenic	<5.7	<5.7	<5.7
Barium	970	280	560
Cadmum	<0.8	<0.8	<0.8
Chromium	100	69	86
Lead	<8	<8	<8
Mercury	NA	NA	NA
Selenium	<6	<6	<6
Silver	<0.1	<0.1	<0.1

*Analysis by inductively coupled plasma emissions spectroscopy.
NA-not analyzed

TABLE 9. MEDIUM-BTU GASIFICATION AND COAL-FIRED POWER PLANT
RCRA LEACHATES OF SOLID WASTES
PERCENT OF TOTAL ELEMENT LEACHED

Contaminant	Lurgi Gasifier Ash	Power Plant Bottom Ash	Power Plant Precipitator Ash
Arsenic	>7.4*	>3.2*	**
Barium	2.5	3.6	1.5
Cadmium	**	**	**
Chromium	6.6	3.8	3.2
Lead	>35*	>12*	>62*
Mercury	NA	NA	NA
Selenium	**	**	**
Silver	**	**	**

NA-not analyzed
*Solid concentration below detection limit.
**All results below detection limit.

CONCLUSIONS

Tables 10 and 11 present the percent of the RCRA elemental contaminants maximum concentration represented by the elemental concentrations in the RCRA leachates of the solid wastes from the coal-fired power plants and gasification processes. There are no values over ten percent, and only five values greater than or equal to five percent. The values above five of the percent of the RCRA contaminants maximum level represented by RCRA leachate concentrations are:

Stanton Plant - Precipitator Ash - Lead	8%
Stanton Plant - Precipitator Ash - Selenium	8.7%
Stanton Plant - Bottom Ash - Lead	6%
Kosovo Power Plant - Precipitator Ash - Lead	5%
Lurgi Gasifier - Gasifier Ash - Chromium	6.6%

The data indicates that the solid wastes tested from the

Wellman-Galusha Gasifier,
Riley Gas Producer,
Stanton Plant (power plant),
Lurgi Gasifier, and
Kosovo Power Plant

processes should be listed as non-hazardous according to the EP toxicity characteristic. Lead in coal-fired power plant precipitator ashes appears to be the single elemental contaminant which contributes most significantly to the toxicity of the RCRA leachates. This may be explained by the theory that lead, being a volatile element, is most probably vaporized during combustion of the coal and condenses upon the precipitator ash as the flue gases cool, thereby enriching the lead concentration in the precipitator ash.

The concentrations of the pesticide and herbicide contaminants in the RCRA leachates of the gasifier ash and cyclone dust from the Riley Gas Producer were not detected by the instrumental analytical method. This data indicates that no pesticides or herbicides, either generated by the process or present in the lignite feedstock, are emitted in gasification solid wastes.

One of the goals of this paper is to present RCRA leachate results developed on solid wastes of coal gasification processes and coal-fired power plants that were using the same feedstock. Table 3 presented proximate and ultimate results and elemental concentrations of the Indianhead lignite collected at the two low-BTU gasifiers and the coal-fired power plant. The proximate and ultimate data indicate that the feedstocks at the three facilities were quite similar. However, the elemental concentrations indicate considerable variability in the three feedstocks with respect to the eight RCRA elemental contaminants.

TABLE 10. LOW-BTU GASIFICATION AND COAL-FIRED POWER PLANT
RCRA LEACHATES OF SOLID WASTES
PERCENT OF RCRA CONTAMINANT MAXIMUM CONCENTRATION

	Wellman-Galusha (Ft. Snelling)		Riley Gas Producer		United Power Assn. Stanton Plant	
Contaminant	Gasifier Ash	Cyclone Dust	Gasifier Ash	Cyclone Dust	Bottom Ash	Precipitator Ash
Arsenic	0.38	0.66	0.66	0.08	0.16	1.4
Barium	1.0	1.0	0.68	0.39	0.30	0.92
Cadmium	<0.7	NA	<0.05	<0.05	0.4	0.5
Chromium	0.02	0.02	<0.02	<0.02	<4	<4
Lead	0.14	0.16	<0.04	<0.04	6	8
Mercury	<0.3	<0.15	<0.25	<0.25	0.15	0.2
Selenium	1.4	0.6	0.6	0.2	<0.4	8.7
Silver	NA	NA	<0.01	<0.01	0.5	0.6

NA - not analyzed

TABLE 11. MEDIUM-BTU GASIFICATION AND COAL-FIRED POWER PLANT RCRA LEACHATES OF SOLID WASTES PERCENT OF RCRA CONTAMINANT MAXIMUM CONCENTRATION

Contaminant	Lurgi Gasifier Ash	Bottom Ash	Precipitator Ash
Arsenic	0.42	0.18	<0.06
Barium	1.2	0.51	0.41
Cadmium	<0.05	<0.05	<0.05
Chromium	6.6	2.6	2.8
Lead	2.8	0.94	5
Mercury	<0.1	<0.01	<0.1
Selenium	<0.4	<0.04	<0.4
Silver	<0.02	<0.02	<0.02

The coal feedstocks of the gasification facility and the coal-fired power plant at the Kosovo site were retrieved from the same stocks, and parameter variabilities of the coal are applicable to both processes.

The data presented in Tables 6 and 9, percent of total element leached by the RCRA extraction procedure, is significantly affected by analytical sensitivities. Of the values not affected by analytical sensitivities, the highest percentages (17-50%) of elements from the solids leached were for cadmium, lead, and selenium in the bottom ash and precipitator ash of the power plant firing Indianhead lignite. The concentrations of these elements were also the highest values measured in the solid wastes; however, no concentration of any of these elements in the RCRA leachates represented as much as ten percent of the RCRA contaminant maximum level. Only one "percent of total element leached" value (Riley Gas Producer cyclone dust - 13.3%) of the RCRA contaminants for the gasification solid wastes exceeded ten percent. These results indicate that the majority of elemental contaminants present in coal gasification solid wastes and coal-fired power plant solid wastes are bound in the solids such that the leachability of the elements is relatively low.

The results of this paper indicate that the solid wastes of specific coal-fired power plants and coal gasification processes tested warrant listing as non-hazardous. However, the non-hazardous listing of these wastes is based upon the characteristic of EP toxicity and primarily upon the elemental contaminants and does not include a severe evaluation of the wastes using other pertinent criteria, such as organic constituents or radioactive components, that may need to be evaluated to determine if there may be a contribution to groundwater contamination. Additional data must be generated to apply the findings of this paper to the solid wastes generated by other coal combustion and coal gasification processes and feedstocks to fully evaluate the status of solid wastes from these industries with regard to Subtitle C regulations.

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CHARACTERIZATION OF SOLID WASTES FROM † INDIRECT LIQUEFACTION FACILITIES

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ABSTRACT

Gasification ash and slag are the major solid wastes generated in indirect coal liquefaction facilities. Smaller amounts of spent catalysts and pollution control sludges may also be generated. There is a limited amount of data on the hazardous and nonhazardous characteristics of these solid wastes. Leachate data for gasifier ash and slag from Lurgi, Wellman-Galusha, and Texaco gasification have been presented elsewhere. The RCRA leaching characteristics of quenched gasifier slag and dust from commercial scale Koppers-Totzek gasification tests in Greece are presented in this paper. The potential accumulation of trace elements in the sludges from biological oxidation of Lurgi gasification condensates are estimated. Koppers-Totzek and Texaco gasification condensates will contain negligible amounts of organics as compared to the Lurgi gasification condensates and will not require biological oxidation. The potential accumulation of trace elements on high temperature shift catalyst are examined as a function of degree of gasification and feed coal characteristics.

1.0 INTRODUCTION

The Resource Conservation and Recovery Act (RCRA) of 1976 directs the Environmental Protection Agency to promulgate regulations to insure the proper disposal of solid wastes for the protection of both human health and the environment. With the recent emphasis on America's coal resources, indirect coal liquefaction may soon be providing a portion of America's energy needs. The The proper disposal of solid wastes generated in the production of liquid fuels and chemicals from coal will be part of the environmental protection required under RCRA. EPA has set forth procedures to determine the potential hazards of solid wastes. Characterization of solid waste streams from indirect liquefaction facilities is the first step toward assuring proper disposal of these wastes.

There is a limited amount of data on the hazardous and nonhazardous characteristics of solid wastes from indirect coal liquefaction facilities. The data are dependent upon the coal used. Leachate data for gasifier ash and slag from Lurgi, Wellman-Galusha, and Texaco gasification have been presented elsewhere.(1,2) The RCRA leaching characteristics of quenched gasifier slag and dust from commercial scale Koppers-Totzek gasification tests in Greece are presented in this paper. The potential accumulation of trace elements in the sludges from biological oxidation of Lurgi gasification condensates is estimated. The potential accumulation of trace elements on high temperature shift catalyst is examined as a function of degree of gasification and feed coal characteristics.

2.0 INDIRECT LIQUEFACTION PROCESSES AND SOLID WASTES

Indirect liquefaction combines coal gasification technologies with catalytic synthesis technologies to produce a range of liquid fuels and chemicals. Figure 1 indicates the basic sequence of process steps necessary for indirect liquefaction. The raw coal is prepared to gasifier feed specifications and gasified (gasification technologies currently in use or under development include the Lurgi, Koppers-Totzek, and Texaco processes). The raw product gas is quenched and upgraded for synthesis by dust removal, shift conversion, and acid gas (e.g., CO_2 and H_2S) removal. The purified synthesis gas is catalytically converted into crude liquid products which can either be used directly as fuels or further refined (synthesis processes currently in use or under development include Fischer-Tropsch, Methanol, and Mobil M gasoline synthesis). Not shown in Figure 1 are the units necessary for on-site steam and power generation, boiler flue gas desulfurization (FGD), oxygen production, raw water treatment, and process cooling.

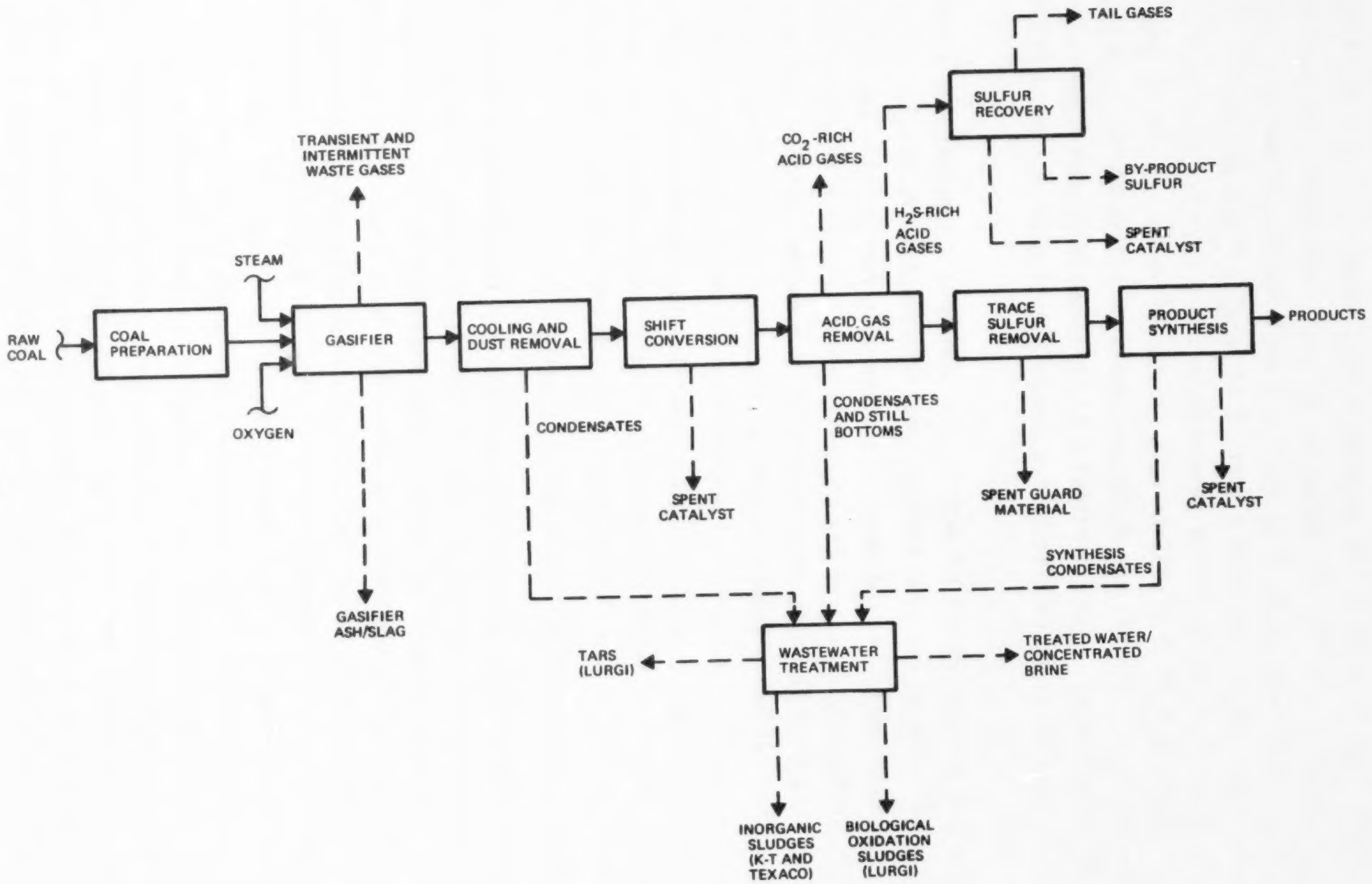
RAW COAL
COAL PREPARATION
STEAM
OXYGEN
GASIFIER
TRANSIENT AND INTERMITTENT WASTE GASES
GASIFIER ASH/SLAG
COOLING AND DUST REMOVAL
CONDENSATES
SHIFT CONVERSION
SPENT CATALYST
ACID GAS REMOVAL
CO2-RICH ACID GASES
H2S-RICH ACID GASES
CONDENSATES AND STILL BOTTOMS
SULFUR RECOVERY
TAIL GASES
BY-PRODUCT SULFUR
SPENT CATALYST
TRACE SULFUR REMOVAL
SPENT GUARD MATERIAL
PRODUCT SYNTHESIS
PRODUCTS
SPENT CATALYST
SYNTHESIS CONDENSATES
WASTEWATER TREATMENT
TARS (LURGI)
TREATED WATER/ CONCENTRATED BRINE
INORGANIC SLUDGES (K-T AND TEXACO)
BIOLOGICAL OXIDATION SLUDGES (LURGI)

Figure 1. Types of Wastes Generated in Indirect Coal Liquefaction Facilities

The major solid waste streams from indirect liquefaction facilities include quenched gasifier ash and slag, gasifier dust, heavy tars and oils, boiler bottom and fly ash, flue gas desulfurization sludge, biological treatment sludges, and sulfur (if not sold as a by-product). Other solid waste streams include spent catalysts, spent sulfur guard, raw water treatment sludges, and chemical precipitation sludges. Leachable trace elements are pollutants of potential concern in all of the solid waste streams. With the exception of the biological oxidation sludges, all of the solid waste streams are inorganic based. The key solid waste streams addressed in this paper are gasifier slag, gasifier dust, biological oxidation sludges, and spent catalysts.

The dry ash Lurgi gasifier operates at temperatures below coal ash fusion temperatures (1815 to 1930°C), while Koppers-Totzek and Texaco gasifiers operate at higher temperatures (2100 to 2600°C). A portion of the coal ash will leave the K-T and Texaco gasifiers as dust entrained in the raw gas stream while the remaining coal ash exits as molten slag from the bottom. Gasifier ash, slag, and dust will consist mainly of nonvolatile and unreacted portions (primarily mineral matter) of the feed coal. Toxic trace elements and substances derived from the parent coal are potential pollutants of concern. Gasifier ash and slag are ordinarily quenched with process water for cooling and/or transportation purposes, and thus will contain substances found in the quench water. Gasifier dust may contain substances found in the wash water.

Biological oxidation sludges result from biological wastewater treatment processes used to treat gasification and synthesis condensates. Nonbiodegradable toxic organic compounds and trace elements derived from gasification and synthesis condensates are the potential pollutants of concern. Koppers-Totzek and Texaco gasification condensates will contain negligible amount of organics as compared to the Lurgi gasification condensates due to the higher combustion temperatures in the Koppers-Totzek and Texaco gasifiers. Lurgi gasification condensates will contain large amounts of dissolved and suspended organics ranging from simple phenols to complex organic acids. Condensates from the Fischer-Tropsch, Methanol, or Mobil M gasoline synthesis section of integrated indirect liquefaction facilities will also contain high loadings of soluble organic pollutants (e.g., alcohols, ketones, organic acids).

There are several types of catalysts which may be used in indirect liquefaction facilities. Shift catalysts include cobalt-molybdate, copper/zinc, and iron chrome based catalysts. Copper/zinc based catalysts are used for Methanol synthesis. Fischer-Tropsch synthesis catalysts are iron based with transition elements as promoters. Zeolites are used for Mobil M gasoline synthesis. Methanation catalysts are nickel based. Certain catalysts are known to contain toxic consituents (e.g., methanation catalysts are nickel-based). High temperature shift catalysts may accumulate toxic constituents through prolonged contact with raw coal gases.

3.0 RCRA HAZARDOUS WASTE CLASSIFICATION CRITERIA

The current Federal hazardous waste regulations define the testing procedures and thresholds which cause a solid waste to be classified as hazardous. A solid waste is considered hazardous if it meets test criteria for ignitability, corrosivity, reactivity, or toxicity. EPA can also list wastes as hazardous if the waste has been found to be fatal to humans in low doses or toxic as indicated by the LD_{50} or LC_{50} levels. Solid wastes containing any of the EPA-specified hazardous constituents* may also be listed as hazardous after taking into consideration some intrinsic factors such as concentration of the constituents in the waste, persistence of the constituent, quantity of wastes, the nature of the toxicity presented by the constituent, and other appropriate factors.

The toxic characteristics of solid wastes are measured by the RCRA Extraction Procedure (EP) Toxicity Test, which is designed to roughly approximate the extraction of soluble material with rain water. The solid is extracted with a sixteen-fold excess of leaching solution at a pH of 5.0 for a 24-hour time period at room temperature. Following the extraction period, the sample is diluted to an aqueous volume of 20 times the sample weight and then filtered to separate the liquid and solid phases. The extract is then analyzed for eight trace elements (arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver) and other identified hazardous constituents which are listed in the Extraction Procedure.(3) The RCRA standards for these eight trace elements are 100 times the Primary Drinking Water Standards.

4.0 CHARACTERISTICS OF INDIRECT LIQUEFACTION WASTES

No indirect coal liquefaction solid wastes are listed as hazardous wastes at the present time. There is insufficient information available at present to determine the hazardous or nonhazardous characteristics of many of the wastes according to RCRA criteria. Some of these wastes are known to contain certain identified constituents of concern (e.g., methanation catalysts are known to contain nickel).

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*There are more than 350 specified hazardous constituents including cyanides, nickel, vanadium pentoxide, phenols, naphthylamines, etc. (see 40 CFR 261, May 19, 1980).

4.1 GASIFIER SLAG AND DUST

The RCRA leachate characteristics of quenched gasifier slag from commercial-scale Koppers-Totzek gasification of Greek Lignite and Illinois #6 coals in Ptolemais, Greece are shown in Table 1.(4) Although the quenched gasifier slag samples were collected under various gasifier operating conditions, the RCRA leachate trace element concentrations are quite uniform. When compared to the RCRA Standard (100 times the primary drinking water standards), none of the samples analyzed would be classified as hazardous. In fact, most of the RCRA leachate trace element concentrations are less than 10 times the primary drinking water standards (selenium concentrations may actually be less than 10 times the primary drinking water standard, but analytical sensitivity is limited in these data). Neutral pH leachate tests on these samples resulted in uniform leachate trace element concentrations similar to those found for the RCRA leachates.(4) The leachate characteristics of the Koppers-Totzek gasifier slag are similar to those presented by other investigators for other coal gasification ashes.(1,2,5)

As with K-T slag, dust from Koppers-Totzek gasification of Greek lignite coal would not be classified as hazardous from a trace element standpoint based on data in Table 2.(4) Most of the RCRA leachate trace element concentrations are less than 10 times the primary drinking water standards (selenium concentrations may actually be less than 10 times the primary drinking water standard, but were not detected as such in these tests). Neutral pH leachate tests on these samples resulted in fairly uniform leachate trace element concentrations with minor differences between the RCRA leachate and neutral pH leachate.(4) There is little difference in the leachate characteristics of gasifier slag and dust disposed of in settling ponds.

The commercial-scale Koppers-Totzek gasification tests with Illinois #6 coal employed a cyclone for dry collection of gasifier dust samples, since the wet sludge from clarification of wash water associated with Illinois #6 coal could not be isolated from that of Greek lignite. In conventional plant designs, the dust is removed from the raw gas in a washer cooler system and this dust would exit the system as solids suspended in the wash water. Some of the toxic

TABLE 1. RCRA LEACHATE CHARACTERISTICS OF QUENCHED KOPPERS-TOTZEK GASIFIER SLAG (GREEK LIGNITE AND ILLINOIS #6 COAL)(4)

	Leachate Trace Element Concentration (mg/l)		
Trace Element	Greek Lignite Coal*	Illinois #6 Coal†	RCRA Standard‡
Ag	<0.01	<0.01	5
As	<0.4	<0.4	5
Ba	0.1	<0.03	100
Cd	<0.007	<0.007	1
Cr	<0.04	<0.04	5
Hg	<0.0002	<0.0002	0.2
Pb	<0.05	<0.09	5
Se	<0.4	<0.4	1

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* Average value obtained from two samples

† Average value obtained from nine samples

‡ 100 times the Primary Drinking Water Standards

TABLE 2. RCRA LEACHATE CHARACTERISTICS OF KOPPERS-TOTZEK GASIFIER DUST DISPOSED IN SETTLING PONDS (GREEK LIGNITE COAL)(4)

	Leachate Trace Element Concentration (mg/l)	
Trace Element	Greek Lignite Coal*	RCRA Standard†
Ag	<0.01	5
As	<0.2	5
Ba	0.38	100
Cd	< 0.007	1
Cr	<0.04	5
Hg	<0.0002	0.2
Pb	<0.05	5
Se	<0.4	1

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*Average value obtained from four samples

†100 times the Primary Drinking Water Standards

components in the gasifier dust would become solubilized in the wash water. Also, toxic components in the wash water could be introduced into the wet dust. The leachate characteristics of dry dust samples from Koppers-Totzek gasification of Illinois #6 coal shown in Table 3(4) are thus a conservative estimate of the leachate characteristics of dust that would be collected in washer cooler systems neglecting the addition of any toxic components that might come from the wash water since some leaching will occur as a result of contact with wash water. The levels of silver, barium, chromium, mercury, and lead are well below the RCRA Standard for classification as a hazardous waste. The arsenic, cadmium, and selenium concentrations are also below the RCRA Standard, but the margin of safety is lower. The neutral pH leachate characteristics are fairly similar to the RCRA leachate characteristics, except for barium and cadmium, which are more readily leached under neutral pH conditions. Although there is no RCRA Standard for boron, its RCRA leachate concentration of 2.2 mg per liter(4) exceeds the irrigation water quality standard of 0.75 mg per liter. Thus, leachability of boron may be an important water quality concern at specific disposal sites even though this element is not considered to be toxic to man or higher animals. It should also be mentioned that the leaching characteristics of the K-T dust do not differ significantly from that of the parent Illinois #6 coal itself.

All available data indicate that gasification ash/slag and dust would be classified as nonhazardous based on the RCRA Extraction Procedure requirements.(1,2) However, it is possible that some of these wastes could be hazardous RCRA if process wastewaters containing leachable toxic substances are used to quench the raw gas or ash.

Leachable trace elements are not the only basis upon which gasifier slag and dust may be listed or classified as hazardous. In the case of both K-T and Texaco gasification dust, leachates may contain substances such as cyanides, sulfides, thiocyanates and ammonia derived from the aqueous condensates or wash waters which have been in contact with dust. Only limited data are currently available regarding the presence and leachability of any such constituents in the "wet" dust from the subject processes.

4.2 BIOLOGICAL OXIDATION SLUDGES

Biological treatment of gasification and synthesis wastewaters is envisioned for many proposed synthetic fuel facilities in the U.S. especially those based upon Lurgi gasification. In these facilities, biological sludges would be generated as a waste from the treatment process. Although there are very limited

TABLE 3. RCRA LEACHATE CHARACTERISTICS OF DRY DUST SAMPLES FROM KOPPERS-TOTZEK GASIFICATION (ILLINOIS #6 COAL)(4)

	Leachate Trace Element Concentration (mg/l)	
Trace Element	Cyclone Dust*	RCRA Standard†
Ag	<0.01	5
As	0.35	5
Ba	<0.02	100
Cd	<0.007	1
Cr	<0.02	5
Hg	<0.0002	0.2
Pb	<0.15	5
Se	0.6	1

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*One sample

†100 times the Primary Drinking Water Standards

leachate and bioassay data available at present on the characteristics of such sludges, the presence of potentially toxic organics (e.g., aromatic amines) and/or trace elements (e.g., Hg, Cd) in the raw wastewaters would suggest that the sludges could be hazardous.

It is possible to estimate the amounts of various trace elements which may accumulate in Lurgi gasification condensate biological oxidation sludges since a limited amount of data are available on the trace element composition of Lurgi gasification condensates.(6,7,8) The accumulation of trace elements in the biological oxidation sludges can be estimated from removal efficiencies achieved for biological treatment of industrial and municipal wastewaters.(9,10,11) The maximum trace element concentrations leachable from Lurgi gasification condensate biological oxidation sludges are estimated in Table 4, assuming that all of the accumulated material is leachable. As indicated in the table, the maxium leachate trace element concentrations may exceed 100 times the Primary Drinking Water Standards. Although barium is not listed in Table 4, it should not be a problem due to its low concentration in the Lurgi raw gas liquor and relatively high RCRA standard concentration. The Lurgi gasification condensate concentrations and biological oxidation removal efficiencies are summarized in the Appendix.

Incineration of biological oxidation sludge has also been proposed for Lurgi facilities to destroy the toxic organics in the waste. However, the incineration residue may also be hazardous due to leachable trace elements, as indicated by calculations in Table 4. The trace element concentrations could be increased by a factor of three or more due to incineration. For these calculations, incineration is assumed to result in a 70 percent reduction in waste quantity (on a dry basis). All of the trace elements present in the biological oxidation sludge are also assumed to accumulate in the incineration residue and to be leachable.

4.3 SPENT CATALYSTS

There is insufficient information available at present to determine the hazardous or nonhazardous characteristics of spent catalysts from indirect liquefaction processes. Due to the proprietary nature of most catalysts, there is little data publicly available on their specific compositions. Some catalysts are known to contain certain identified hazardous constituents (e.g., methanation catalysts are nickel-based). However, many catalysts are presumed to not contain any hazardous constituents (e.g., Mobil M gasoline synthesis and Claus

TABLE 4. PREDICTED RCRA LEACHATE CHARACTERISTICS OF SLUDGE FROM BIOLOGICAL OXIDATION OF LURGI GASIFICATION CONDENSATES, WORST CASE

	Predicted Maximum Leachate Trace Element Concentration (mg/l)		
Trace Element	Biological Oxidation Sludge	Incineration Residue	RCRA Standard*
Rosebud Coal			
Ag	5.5	18.2	5
As	0.5	1.8	5
Cd	4.1	13.8	1
Cr	54.5	181.8	5
Hg	2.4	7.9	0.2
Pb	5.5	18.2	5
Se	2.9	9.7	1
Illinois #6 Coal			
Ag	5.8	19.2	5
As	0.9	2.9	5
Cd	4.4	14.6	1
Cr	172.8	576.1	5
Hg	30.0	99.9	0.2
Pb	172.8	576.1	5
Se	23.0	76.8	1
Dunn Lignite Coal			
Ag	7.2	24.0	5
As	53.9	179.8	5
Cd	0.8	2.7	1
Cr	1.1	3.6	5
Hg	1.4	4.7	0.2
Pb	7.2	24.0	5
Se	115.1	383.6	1

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*100 times the Primary Drinking Water Standards catalysts which are zeolite- and alumina-based catalysts, respectively).

Although fresh catalysts may not contain any toxic constituents, they may accumulate such constituents through prolonged contact with the coal gases. In particular, potentially volatile trace elements originally present in the feed coal (e.g., As, Cd, Cr, Hg, Pb, and Se) may accumulate in the sulfur tolerant shift catalyst over time, since this type of catalyst is directly exposed to hot raw gas and is known to have an affinity for various trace elements.(12,13) There is essentially no leachate data available in the public domain on any of the catalysts used in indirect liquefaction processes.

The potential accumulation of various trace elements on the shift catalyst could be estimated based on the trace element composition of the raw coal gas, however, sufficient data are not available. Some data are available to allow indirect calculation of the degree of gasification of several trace elements in various gasifiers, although a wide range of values can be derived depending on which set of data are used.(14,15) For purposes of this paper, therefore, the accumulation of trace elements on shift catalyst have been estimated as a function of degree of gasification and feed coal characteristics. Table 5 summarizes the trace element contents of American coals.

Assuming all of the gaseous trace elements are deposited on by the shift catalyst and are subsequently leachable, the time required for shift catalyst to become hazardous due to trace element deposition can be estimated. Figures 2 to 4 show the results as a function of trace element concentration in the coal and percent of the trace element gasified. Shift catalysts is estimated to become hazardous within twelve hours under the worst case (i.e., 100 percent gasification) for coals with the mean concentrations of the trace elements shown in Table 5. The nonhazardous lifetime would be increased to about 3 months when only one percent gasification of the trace elements occurs. Minimum trace element levels found in American coals would still result in a hazardous catalyst within a week if 100 percent of the trace elements are gasified. The nonhazardous lifetime of the shift catalyst would be increased to about 3 years when only one percent gasification of the trace elements occurs.

Although there are large uncertainties in the exact levels of various elements which would accumulate on the shift catalyst, the calculations presented indicate a reasonable potential for the spent catalyst to become hazardous. Also, shift catalyst may be affected by trace elements in terms of activity. Elements

TABLE 5. TRACE ELEMENT CONTENTS OF AMERICAN COALS(14,15)

Trace Element	Concentration in Coal (ppm)		
	Mean	Minimum	Maximum
As	16.4	0.5	357
Cd	1.8	0.02	100
Cr	15.3	<0.5	70
Hg	0.17	0.01	3.3
Pb	21.2	<0.7	283
Se	3.6	<0.10	150

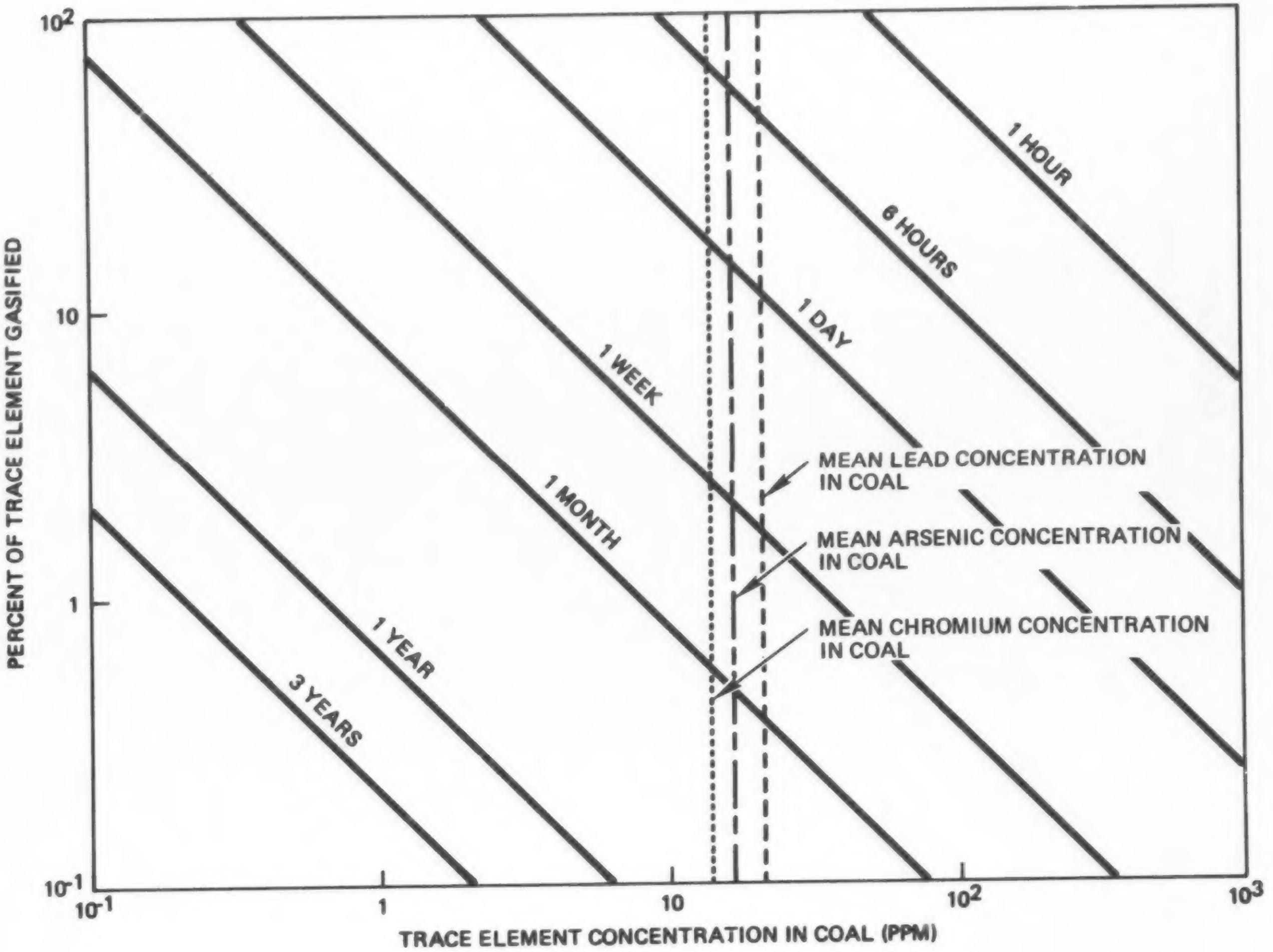

Figure 2. Predicted Shift Catalyst Lifetime Required to Reach RCRA Leachate Standards for As, Cr, and Pb (5 mg/l) *

* (BASED ON 2 KG RAW COAL GAS PER HOUR PER KG CATALYST)

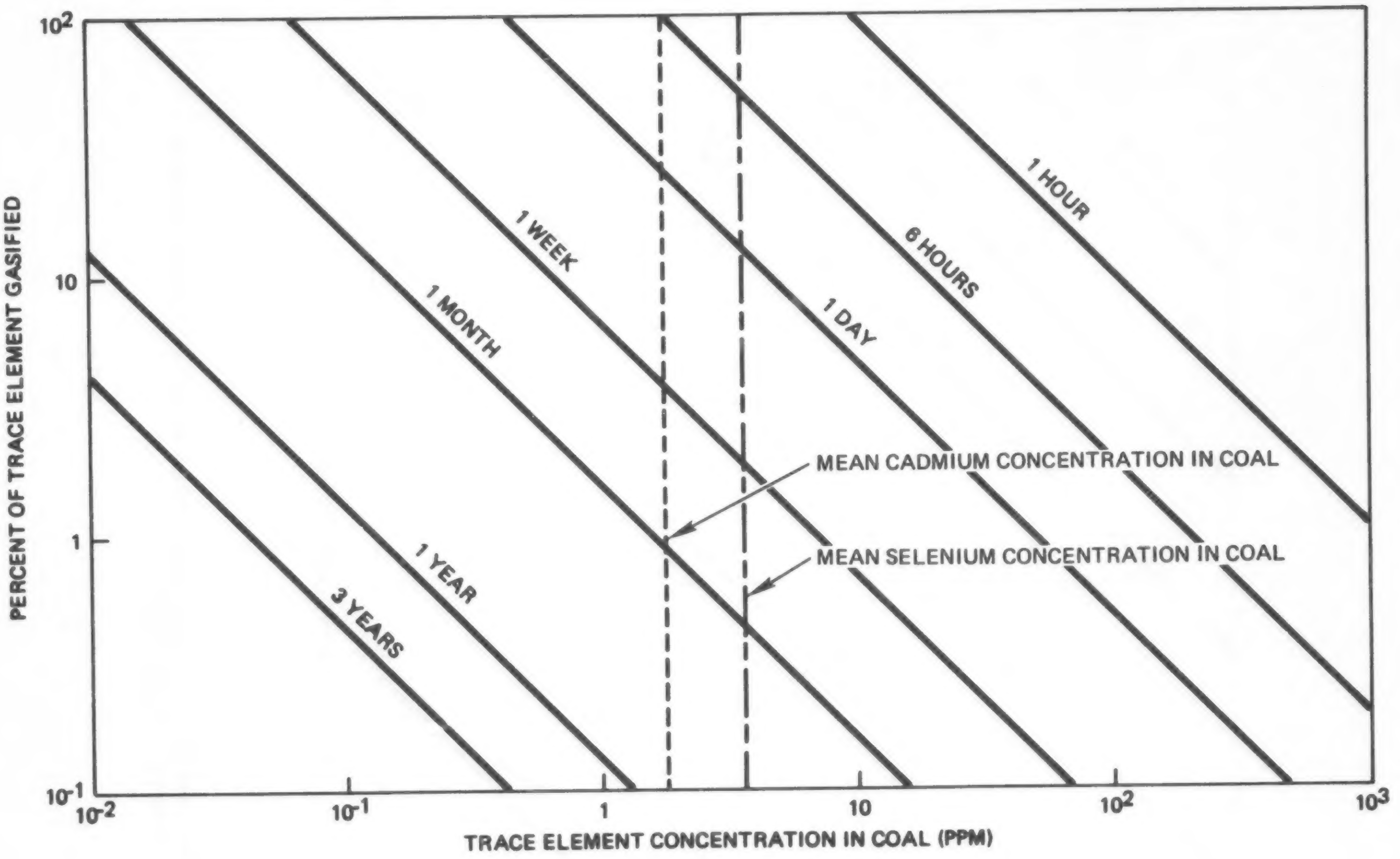

Figure 3. Predicted Shift Catalyst Lifetime Required to Reach RCRA Leachate Standards for Cd and Se (1 mg/l) *

* (BASED ON 2 KG RAW COAL GAS PER HOUR PER KG CATALYST)

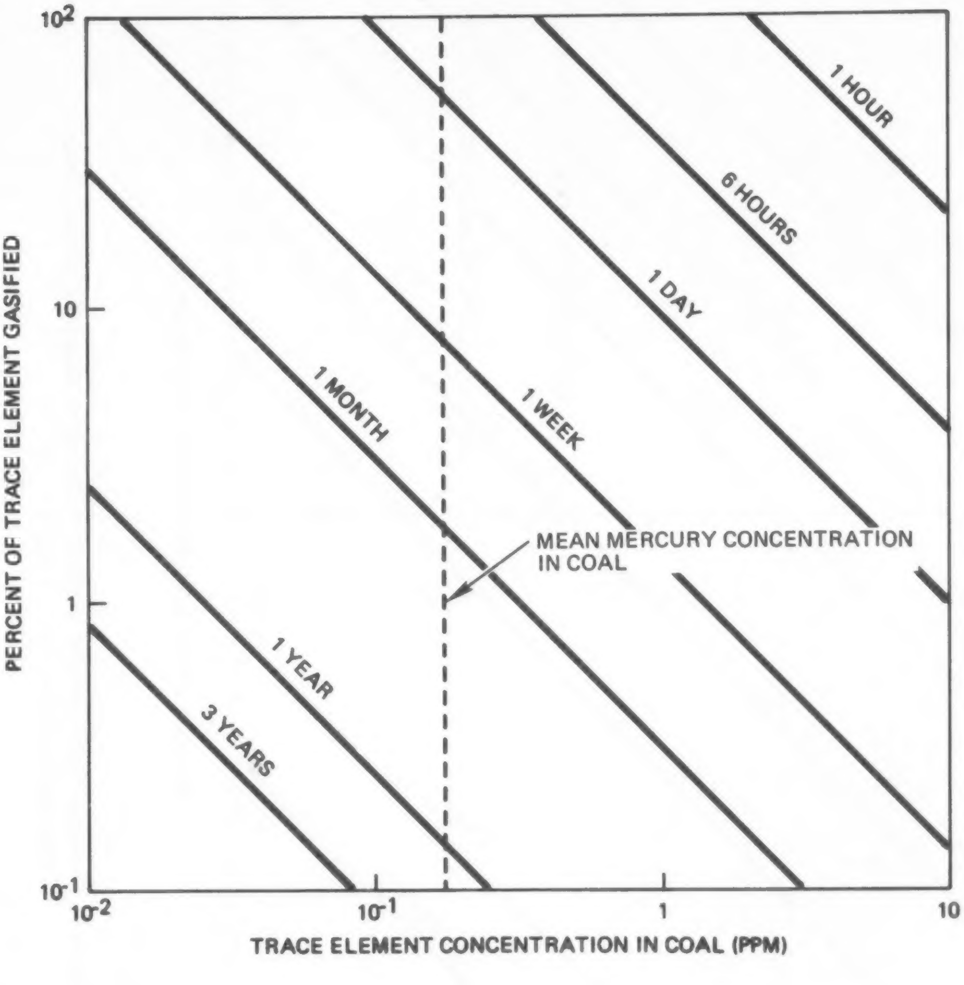

Figure 4. Predicted Shift Catalyst Lifetime Required to Reach RCRA Leachate Standard for Hg (0.2 mg/l) *

* (BASED ON 2 KG RAW COAL GAS PER HOUR PER KG CATALYST)

such as As, Pb, Cr, Hg, and Cd are likely to be catalyst poisons at some levels, and hence catalyst life could actually be shorter than that found in non-coal applications due to deactivation by trace element accumulation. Process designers should be aware of the potential for catalyst deactivation by coal derived trace elements. Finally, it should be mentioned that many catalysts contain metals of commercial value and hence may not have to be viewed as wastes if these metals are reclaimed.

5.0 CONCLUSIONS

(1) Commercial-scale Koppers-Totzek gasification tests with Greek lignite and Illinois #6 coals in Ptolemais, Greece indicate that quenched gasifier slag and dry or wet dust would not be classified as hazardous based upon RCRA leachate criteria for trace elements. However process or wastewaters used to cool or quench solids may introduce toxic constituents.

(2) Calculations indicate that maximum trace element concentrations leachable from Lurgi gasification condensate biological oxidation sludges may exceed 100 times the Primary Drinking Water Standards. Although incineration of the biological oxidation sludge is expected to destroy the toxic organics in the sludge, the incineration residue may still be hazardous.

(3) Certain spent catalysts (e.g., nickel based methanol or methanation catalysts) are expected to be inherently hazardous. High temperature shift catalysts may become hazardous due to accumulation of leachable trace elements through prolonged contact with coal gases.

6.0 RECOMMENDATIONS

(1) Additional RCRA leachate data for gasifier ash and slag produced by various gasification technologies using several coals would be helpful to verify the nonhazardous characteristics of the ash and slag. The presence of toxic organic or inorganic compounds in ash quenched with process wastewater could be indicated by both chemical analyses and bioassay testing of solids and/or leachates.

(2) RCRA leachate data should be collected to determine the hazardous or nonhazardous characteristics of biological oxidation sludges from wastewater treatment. Performance of bioassay tests would

provide information on the trace elements and the nonbiodegradable but toxic organics that might be present in these sludges.

(3) Obtaining RCRA leachate and bioassay data on fresh catalysts would allow determination of the hazardous and nonhazardous characteristics of the basic catalyst materials. RCRA leachate and bioassay data on spent catalysts would provide insight into the potential accumulation of trace elements or toxic organics through contact with coal derived gases.

APPENDIX

EXPECTED CHARACTERISTICS OF LURGI GASIFICATION CONDENSATES

	Rosebud Coal(6)	Illinois #6 Coal(6)	Dunn Lignite Coal(7,8)
Trace Elements (mg/ℓ)			
Ag	0.3	0.1	<0.2
As	0.06	0.03	3
Ba	<0.01	<0.1	--
Cd	0.3	<0.1	0.03
Cr	3	8	<0.03
Hg	0.1	0.4	<0.03
Pb	0.3	3	0.2
Se	0.1	0.25	2
Raw Gas Liquor Production Rate (1000 kg/hr)	304	507	441
Biological Oxidation Sludge Production Rate (kg/hr)	1900	1000	1400

Design Basis - 2.5×10^{10} kcal/day energy output from Methanol Synthesis

BIOLOGICAL OXIDATION REMOVAL EFFICIENCIES

Trace Element	Percentage Removal	Reference
Ag	50	(9)
As	25	(10)
Cd	38	(10)
Cr	50	(11)
Hg	65	(11)
Pb	50	(11)
Se	80	(11)

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ASH/SLAG RESIDUALS AND WASTEWATER TREATMENT PLANT SLUDGES FROM SYNFUELS FACILITIES: CHARACTERIZATIONS AND IMPLICATIONS FOR DISPOSAL

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ABSTRACT

The purpose of this paper is to present an overview of research conducted at the University of Pittsburgh in the area of coal conversion ash and slag. Residuals were obtained from the GFETC "slagging Lurgi type" gasifier (two different runs), METC (Wellman-Galusha type) pressurized gasifier, DOE-Chapman gasifier fly ash, and two H-Coal vacuum bottoms residuals. A first screen bioassay of SRC-II Fort Lewis coal liquefaction residuals and sludges is also presented. In addition, research has been conducted at the University of Pittsburgh for the past few years in the area of developing a stable pretreatment and biological treatment facility for the processing of phenolic type coal gasification wastewaters. During the processing of wastewaters, sludges are produced which are assessed for toxicity, mutagenicity and overall disposability characteristics.

OVERVIEW OF RESULTS

It may be expected that a commercial sized coal conversion facility will produce a variety of solid waste residuals. The wastes generated that may exert the greatest influence on residuals management are: (1,2)

1. COAL PREPARATION PLANT RESIDUALS-to include coal refuse, coal dust and wastewater from the tailing pond

2. COAL GASIFICATION PLANT AREA WASTES-to include residual ash, slag and quench waters

3. STEAM AND POWER PLANT GENERATION WASTES-to include residual ash flue gas desulfurization sludge

4. RAW WATER TREATMENT AREA-to include sludge from solids in the raw water source

5. WASTEWATER TREATMENT PLANT AREA SLUDGES-to include lime sludge, organic sludge, waste biological sludges and oil and tar residuals

6. TAR SEPARATION AREA

7. PHENOL REMOVAL AREA-to include filter backwash and sludges containing phenolics when solid extraction processes are used

8. SULFUR REMOVAL AREA SLUDGES-to include elemental or product sulfur if nonsaleable or stored on site

9. TAILGAS TREATMENT AREA SLUDGES-to include residual sludge materials.

Land disposal of solid residuals is an economically logical choice for an overall management scheme of commercial scale synthetic fuel facility solid wastes. Such land disposal, however, must be done in an environmentally and "RCRA" acceptable manner. Bern et al.(1) have outlined management alternatives that are available to owners of commercial sized synthetic fuels facilities.

Neufeld et al.(2) have reported on chemical and biological properties of coal conversion ash residuals derived from U.S. DOE sponsored large scale coal gasification and direct liquefaction facilities. Characterizations of such solid wastes include proximate analysis, development of natural particle sized distributions, and heavy metal analysis of leachates from each sized fraction. This work showed that the smaller sized fractions yield much greater quantities of heavy metals in derived leachates. In no case did resulting leachates using the EPA "EP" procedures and ASTM-A distilled de-ionized water leaching procedures yield concentrations in excess of one hundred times the concentration of primary drinking water heavy metals; a value above which wastes are determined to be "hazardous". In addition, no coal conversion waste ash or slag residual gave positive result in Ames testing. On the other hand, evidence of Daphnia toxicity was observed in some coal conversion derived leachates.

Wastewater treatment sludges were generated as part of our study of METC gasifier effluent control technology development. Wastewater treatment plant sludges that were studied include lime sludges developed from pH adjustment prior to ammonia stripping, organic sludges developed by filtration and precipitation prior to biological oxidation, and biological sludges from the treatment of fixed bed coal gasification wastewater. Leachates from such sludges are shown to be toxic to Daphnia magna while negative results were observed in Ames testing.

DESCRIPTION OF COAL CONVERSION SOLID RESIDUALS

CHAPMAN (WILPUTTE) GASIFIER

The Chapman fixed bed dry bottom gasification facility at Kings Port, Tennessee produces a low BTU product gas used for combustion fuel. Gas cleaning and purification operations involve cyclone removal of dry particulates and aqueous gas quenching. Solid wastes coming from this facility are gasifier and cyclone ash with cyclone ash being used in our experimental procedures. It should be noted that cyclone ash differs inherently from the more familiar coal combustion facility fly ash in that gasifier particulates have gone through a reducing zone as compared to coal combustion fly ash particulates which go through an oxidizing zone.

GRAND FORKS ENERGY TECHNOLOGY CENTER

The Grand Forks Energy Technology Center has a "Lurgi type" oxygen blown slagging gasifier. Two samples were obtained from this facility, the first being a brown colored slag from run #R-52 using Indian-Head lignite coal, the second being a black colored slag obtained from run #RA-93.

MORGANTOWN COAL CONVERSION FACILITY

The Morgantown Energy Technology Center gasifier is a pressurized "Wellman-Galusha" type of system. The solid waste material obtained was bottom ash/slag from the gasifier when operated using a bituminous coal and was composed of principally large (2") particle sizes.

H-COAL LIQUEFACTION WASTES

The H-Coal process is a direct liquefaction facility developed by Hydrocarbon Research Incorporated. The two H-Coal solid waste samples obtained were both vacuum still bottoms from the direct liquefaction step. One sample was generated from Illinois coal when the system was operated in the "syncrude" mode, while the second sample was generated from Illinois coal when operated in the "fuel oil" mode. These samples will be referred to as "H-Coal #3" and "H-Coal #4". Both H-Coal samples were irregularly shaped black "chunks" of materials with a majority of chunks larger than three inches by three inches.

WASTEWATER SLUDGE SAMPLES

Figure 1 is a flow diagram of the research pretreatment and biological treatment steps associated with the processing of METC coal gasification wastewaters as conducted at the University of Pittsburgh. Wastewater was provided to the University from the hot gas quench of the stirred fixed bed gas producer located and operated by METC. The goal of the treatment processes at the University of Pittsburgh were to develop a linkage of operations that could effectively treat coal conversion wastewaters in a stable fashion. Stability for the bioreactor was defined as occurring when at least three sludge ages had passed.

Table 1 is a characterization of three different shipments of METC wastewaters. The first shipment represents a "nontypical sample" produced at least one year earlier to our testing while the second sample was "more typical" being produced within several months of our evaluations. Sludges for this study are generated from the "typical" wastewater sample.

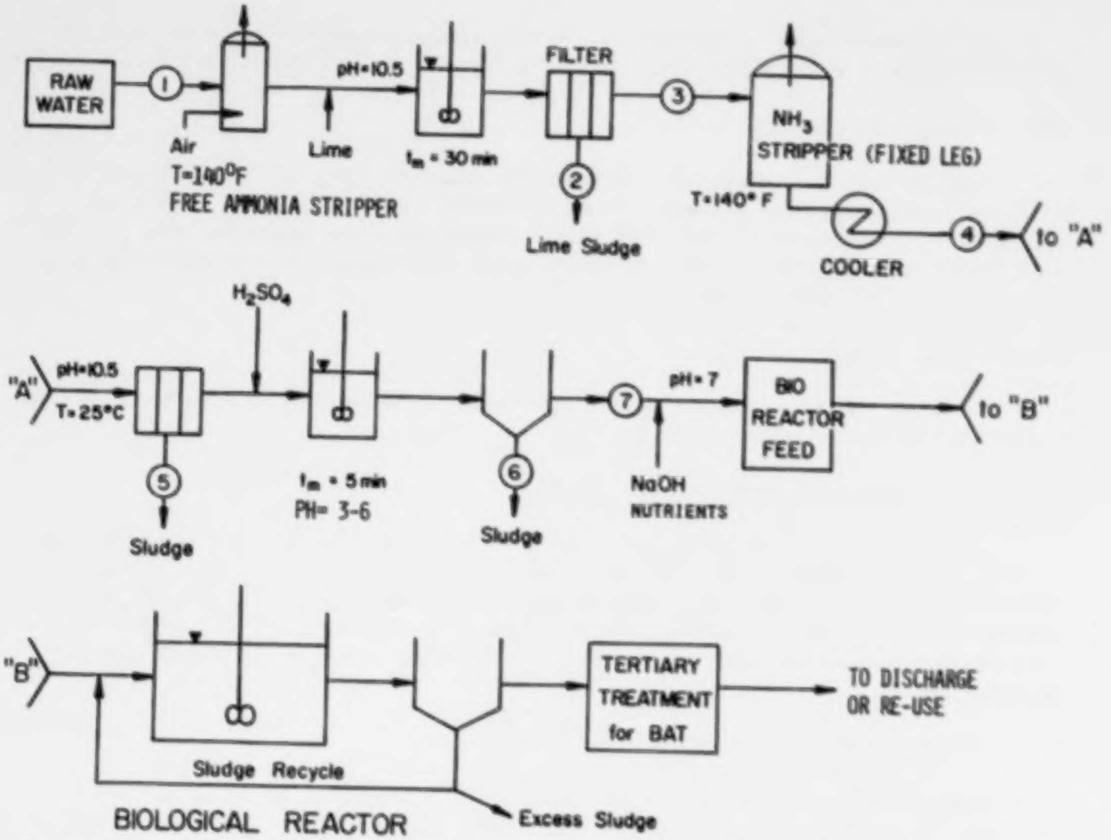
RAW WATER
1
Air
T=140°F
FREE AMMONIA STRIPPER
Lime
pH=10.5
t_m = 30 min
FILTER
2
Lime Sludge
3
NH_3 STRIPPER (FIXED LEG)
T=140° F
COOLER
4
to "A"
"A"
pH=10.5
T=25°C
5
Sludge
H_2SO_4
t_m = 5 min
PH= 3-6
6
Sludge
7
pH=7
NaOH
NUTRIENTS
BIO REACTOR FEED
to "B"
"B"
Sludge Recycle
BIOLOGICAL REACTOR
Excess Sludge
TERTIARY TREATMENT for BAT
TO DISCHARGE OR RE-USE

Figure 1. METC Gasifier Wastewater Process Flow Diagram

TABLE 1. METC WASTEWATER CHARACTERIZATION

ITEM	SHIPMENT #1 (AGED SAMPLE) CONCENTRATION	SHIPMENT #2 RUN 94 CONCENTRATION	SHIPMENT #3 RUN 95 CONCENTRATION
Phenol	970 mg/L	2,375 mg/L	3,750 mg/L
COD	53,024 mg/L	13,350 mg/L	12,750 mg/L
TOC	14,102 mg/L	5,374 mg/L	5,390 mg/L
TIC	30 mg/L	242 mg/L	4,350 mg/L
Total Residue	72,334 mg/L	1,349 mg/L	4,420 mg/L
Fixed Residue	1,334 mg/L	143.2 mg/L	630 mg/L
Volatile Residue	71,000 mg/L	1,205.8 mg/L	3,790 mg/L
Freon Sol. Oil & Grease	356 mg/L	1,495.0 mg/L	----
Acetone Sol. Oil & Grease	1,633 mg/L	106.3 mg/L	----
pH	7.5	8.0	8.8
Alkalinity (pH 4.5)	2,100 mg/L	23,750 mg/L	21,855 mg/L
SCN	----	372 mg/L	----
NH_3	11,000 mg/L	3,200 mg/L	7,000 mg/L
Phenol/TOC ratio	.069	.44	.70

The pretreatment train used to treat coal conversion waters, and to develop sludges within our laboratory represent a linkage of steps as follows:

Step 1-Free Ammonia Leg

This is accomplished in a laboratory via aerating a 15 to 20 gallon batch of wastewater at a temperature of 60°C. Such aeration liberates noticeable quantities of H_2S, volatile organics, free ammonia, and results in a reduction in the overall alkalinity of solution, thus minimizing lime requirements for the fixed leg.

Step 2-Lime Addition

Lime (as CaOH) is added to the wastewater in sufficient quantities to bring the pH to a range of 10 to 11.

Step 3-Filtration to Remove Lime Sludge

A large Buchner funnel with coarse grade filter paper is utilized to remove precipitated lime. The resultant sludge is brown in color, and contains organic materials. This sludge, referred to as "lime sludge", was subsequently dried and leached in accordance with the EPA "EP" and ASTM-A extraction procedures and tested for heavy metal content and toxicity to *Daphnia magna*.

Step 4-Fixed Leg Ammonia Stripping

Ammonia is stripped at 140°F and pH 10½ batchwise in a 15 gallon stripper to simulate commercial scale fixed leg ammonia stripping. The wastewater is kept in the ammonia stripper until the total ammonia in solution reaches about 100 mg/l. The wastewater is then removed from the ammonia stripper and placed into a large glass jar where it is subsequently air cooled.

Step 5-Filtration

After ammonia stripping, the wastewater is pH adjusted using sulfuric acid. Polymerization of trace organics appears to take place in the stripper thus resulting in an organic sludge formation which is filtered out prior to subsequent biological oxidation. Our approach is to remove the maximum quantity of organics possible prior to biological oxidation via judicious pH adjustment, flocculation and filtration. This sludge, called an "alum sludge" (due to the addition of alum to promote coagulation/floculation) was also tested in this study for leachate evaluations using *Daphnia magna* and atomic adsorption spectrosocopy.

Step 6-Biological Reaction Phase

Pretreated wastewater is diluted as desired and fed on a continuous basis to completely mixed activated sludge type bio-reactors with hydraulic detention times of 1.0 days and sludge ages in the range of 20 days. During one of our studies, a maximum of 60% wastewater diluted with tap water was utilized. Phase II of our present study is an attempt to minimize dilution water requirement in the biological reaction phase. Biological sludges harvested from the activated sludge reactors are being subjected to Ames testing, Daphnia toxicity testing and extensive chemical evaluations during the current phase of study.

PHYSICAL/CHEMICAL ANALYSIS OF ASH/SLAG SOLID WASTE RESIDUALS

All samples, with the exception of the lime and alum sludges from the wastewater treatment train, were subjected to particle size distribution analysis without altering the nature of samples. The philosophy of this approach was to more properly reflect that which would be placed in landfill systems; thus, crushing and grinding were not done. H-Coal samples were subjected to crushing and grinding because of the rather large chunks of materials received.

All sieving was conducted with U.S. standard sieves #'s 10, 20, 40, 60, 100 and 200 for sufficient duration to collect enough sample of each size fraction as required for leaching tests.

Samples of each of the mesh sizes were subjected to leaching via the ASTM-A leaching procedure and current EPA-EP leaching test and a self designed "University of Pittsburgh" procedure using pH=2 HNO_3. A portion of the leachates were segregated for heavy metal AA analysis, and Daphnia magna evaluations.

DAPHNIA TOXICITY EVALUATIONS

Acute toxicity testing was conducted on generated sludge using Daphnia magna standarized procedures outlined in Standard Methods, and in draft ASTM procedures. It should be noted, however, that all samples of leachates were adjusted to a pH between 7.4 and 7.6 before being subjected to the Daphnia magna testing. The philosophy of our approach is not to evaluate the toxicity of H^+ and OH^-, but rather than to evaluate the toxicity of constituents contained in the leachates. Figure 2 is a typical plot of data showing conductivity of GFETC lignite slag leachates as a function of particle size of solid waste. As may be seen from this figure, smaller particle sizes tend to leach greater quantities of dissolved materials than larger particles. The differences in conductivity value from one test to another is a function of water to solid ratio and additives specific to each leaching procedure.

Table 2 is a summary of GFETC solid waste heavy metal constituents in leachates as a function of the leaching test procedures also showing smaller particle sizes leaching greater quantities of specific key metals. For comparison purposes, table 3 list results of leaching tests using "H-Coal #3" solid waste samples. Similar data was developed for the H-Coal #4, METC and Chapman leachates, as was done to the GFETC leachates. Table 4 is a summary of the compositional results of leaching of lime and alum sludges produced from the treatment of METC gasification wastewaters.

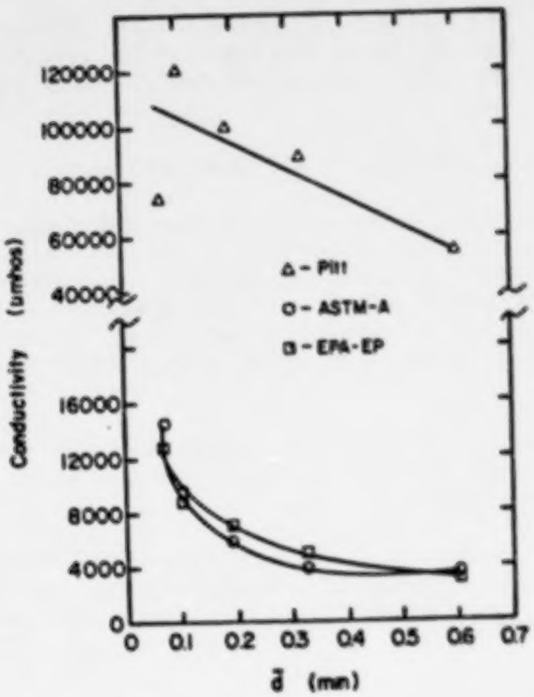

Figure 2. Conductivity Data - GFETC NO. 1
(Gasifier Bottom Slag from RA-52 Using Lignite Coal)

TABLE 2. RESULTS OF LEACHING TESTS - GFETC
(GASIFIER BOTTOM SLAG FROM RA-52 UAING LIGNITE COAL

Metal Concentrations (all units mg/l)

Test Procedure	Mesh Size	pH	Ag	Be	Ca	Cd	Cr	Cu	Fe	Mg	Mn	Pb	Zn
ASTM-A	20-40	9.62	0	0	196	0	0	0	0	1.7	0	0	0.1
ASTM-A	40-60	9.25	0	0	220	0	0	0	0	1.8	0	0	0.1
ASTM-A	60-100	9.01	0	0	300	0	0	0	0	1.8	0	0	0.3
ASTM-A	100-200	8.80	0	0	380	0	0	0	0	2.1	0	0	0.4
ASTM-A	<200	8.58	0	0	580	0	0	0	0	2.2	0	0	0.7
EPA-EP	20-40	4.97	0	0	344	0	0	0	84	75	0.8	0	0.3
EPA-EP	40-60	4.98	0	0	540	0	0	0	96	90	1.6	0	0.3
EPA-EP	60-100	5.44	0	0	800	0	0	0	165	100	1.8	0	0.4
EPA-EP	100-200	5.66	0	0	1140	0	0	0	78	105	2.9	0	0.4
EPA-EP	<200	5.76	0	0	1440	0	0	0	93	105	5.3	0	0.9
PITT	20-40	2.03	0	0	2870	0	0	0	420	1200	2.9	0	0.7
PITT	40-60	1.70	0	0.5	4800	0	0	0	540	1900	4.4	0	1.3
PITT	60-100	1.64	0	0.5	5400	0	2.5	0	680	2200	5.0	1.5	1.4
PITT	100-200	1.69	0	0.8	6400	0	3.7	0	1040	2940	8.0	1.5	2.3
PITT	<200	1.74	0	0.5	3920	0	3.7	52.8	2150	1700	10.5	1.5	39.0

TABLE 3. RESULTS OF LEACHING TESTS - H-COAL #3
(LIQUEFACTION VACUUM STILL BOTTOMS FROM SYNCRUDE MODE USING ILLINOIS COAL)

Metal Concentrations (all units mg/l except Hg - ug/l)

Test Procedure	Mesh Size	pH	Ag	Ba	Ca	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Pb	Zn
ASTM-A	20-40	11.03	0	0	130	0	0	0	0	0.6	0.2	0	0	0
ASTM-A	40-60	11.22	0	0	160	0	0	0	0	0.3	0.3	0	0	0.1
ASTM-A	60-100	11.33	0	0	190	0	0	0	0	0.6	0.4	0	0	0.1
ASTM-A	100-200	11.48	0	0	300	0	0	0	0	0.3	0.4	0	0	0.3
ASTM-A	<200	11.49	0	0	370	0	0	0	0	0.3	0.3	0.2	0	0.6
EPA-EP	20-40	4.96	0	0	150	0	0	0	1.1	0	1.0	1.0	0	0
EPA-EP	40-60	4.90	0	0	220	0	0	0	2.0	0	1.2	1.4	0	0
EPA-EP	60-100	4.88	0	0	320	0	0	0	3.4	0	1.7	2.3	0	0.1
EPA-EP	100-200	4.87	0	0	400	0	0	0	4.8	0.3	2.0	2.9	0	0.3
EPA-EP	<200	4.91	0	0	420	0	0	0	4.8	0	2.0	2.9	0	0.4
PITT	20-40	1.72	0	0	194	0	0	0.9	7.0	0.3	1.4	1.2	0	0.3
PITT	40-60	1.74	0	0	270	0	0	1.3	10.0	0	1.7	1.6	0	0.3
PITT	60-100	1.76	0	0	340	0	0	1.3	15.0	0.3	1.9	2.3	0	0.4
PITT	100-200	1.77	0	0	430	0	0	1.3	33.0	0.3	4.8	3.1	0	0.4
PITT	<200	1.71	0	0	410	0	0	1.3	32.0	0.3	5.5	2.9	0	0.4

TABLE 4. RESULTS OF LEACHING TESTS - LIME AND ALUM SLUDGES
(FROM TREATMENT OF METC WASTEWATER

Concentrations (all units mg/l)*

Material	Test Procedure	pH	Ca	Cd	Cu	Fe	Mg	Zn	Conductivity (umhos)	TOC (mg/l)	Phenol (mg/l)
LIME	ASTM-A	11.84	640	0	0	1.4	0.1	0	4800	1590	720
LIME	EPA-EP	7.29	1630	0.1	0	0.8	26	0.2	6400	2030	133
ALUM	ASTM-A	7.75	340	0	0	7.0	176	0	5300	1960	1530
ALUM	EPA-EP	6.92	1800	0	0.3	0.8	26	0.4	7100	2080	455

*Ag, Be, Cr, Mn, Pb below detectable limits

Figure 3 is a plot of Daphnia toxicity information for leachates derived from the EPA-"EP" extraction procedures utilizing the smallest and largest particle sizes of GFETC solid waste residuals. The 48 hour LC-50 values for the largest particle size is 8.9% dilution, while for the smallest particle size, is 7.0% dilution. In a summary of LC-50 data on table 5, ASTM-A distilled water leaching protocol always showed LC-50 values on the order of 100% dilution with lower values for the EPA-EP test. It may thus be concluded that the inherent nature of the EPA-"EP" procedure using acetic acid causes Daphnia toxicity, thus raising questions as to the validity of the application of Daphnia toxicity testing to leachates produced in accord with the EPA approach. Evaluation, however, of Daphnia toxicity to acetic acid reagents as used in the EPA extraction procedure test where no solid wastes are leached (after neutralization) show the LC-50 value to be 85% in concentration and thus do not explain the total toxicity of EPA leachates of solid wastes to Daphnia. It was noted from this and a series of similar tests, that results using EPA extraction procedure protocols appear far more toxic to Daphnia in all cases than results using the ASTM-A "distilled water" approach.

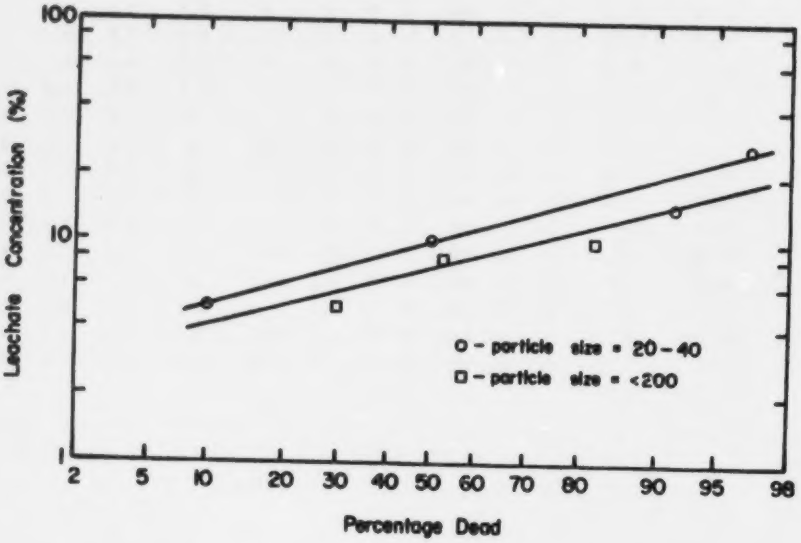

Figure 3. Daphnia Toxicity Data From GFETC NO. 1 EPA-EP LEACHATES

TABLE 5. RESULTS OF DAPHNIA MAGNA TOXICITY TESTING

Material	Test Procedure	Mesh Size	48hr LC50 %	95% Confidence Limits UCL	LCL
CFA	ASTM-A	20-40	>100	--	--
CFA	ASTM-A	<200	>100	--	--
CFA	EPA-EP	20-40	2.9	3.4	2.4
CFA	EPA-EP	<200	4.8	5.8	3.9
H-COAL #4	ASTM-A	20-40	>100	--	--
H-COAL #4	ASTM-A	<200	>100	--	--
H-COAL #4	EPA-EP	20-40	2.0	2.5	1.6
H-COAL #4	EPA-EP	<200	1.8	2.3	1.4
H-COAL #3	ASTM-A	20-40	>100	--	--
H-COAL #3	ASTM-A	<200	>100	--	--
H-COAL #3	EPA-EP	20-40	22	27	18
H-COAL #3	EPA-EP	<200	23	29	18
GFETC #1	ASTM-A	20-40	>100	--	--
GFETC #1	ASTM-A	<200	>100	--	--
GFETC #1	EPA-EP	20-40	8.9	11.1	7.1
GFETC #1	EPA-EP	<200	7.0	8.0	6.1
GFETC #2	ASTM-A	< 60	>100	--	--
GFETC #2	EPA-EP	< 60	11.2	12.6	9.9
METC	ASTM-A	> 10	>100	--	--
METC	ASTM-A	< 60	>100	--	--
METC	EPA-EP	> 10	0.28	0.37	0.20
METC	EPA-EP	< 60	0.12	0.17	0.09
LIME SLUDGE	ASTM-A	--	1.4	1.6	1.2
LIME SLUDGE	EPA-EP	--	4.3	5.2	3.6
ALUM SLUDGE	ASTM-A	--	0.74	0.82	0.67
ALUM SLUDGE	EPA-EP	--	1.6	1.7	1.4
ACID CONTROL	---	--	85	95	76

Table 5 also indicates that Daphnia, toxicity to wastewater treatment sludge leachates are far more toxic than leachates produced from gasification bottom ash or slag residuals. As one illustration, figure 4 is a plot of Daphnia toxicity from leachates produced from lime sludges generated from the waste treatment scheme when processing METC fixed bed coal conversion wastewaters. As can be seen, despite the numerical difference of results when leaching via the EPA or the ASTM-A approach, toxicities of waste treatment plant sludges are considerably greater than toxicities of ash/slag leachates. It should be noted, however, that in no case did primary drinking water heavy metals exceed 100 times drinking water standards; thus implying that such sludges are not to be considered as hazardous in a "RCRA" context.

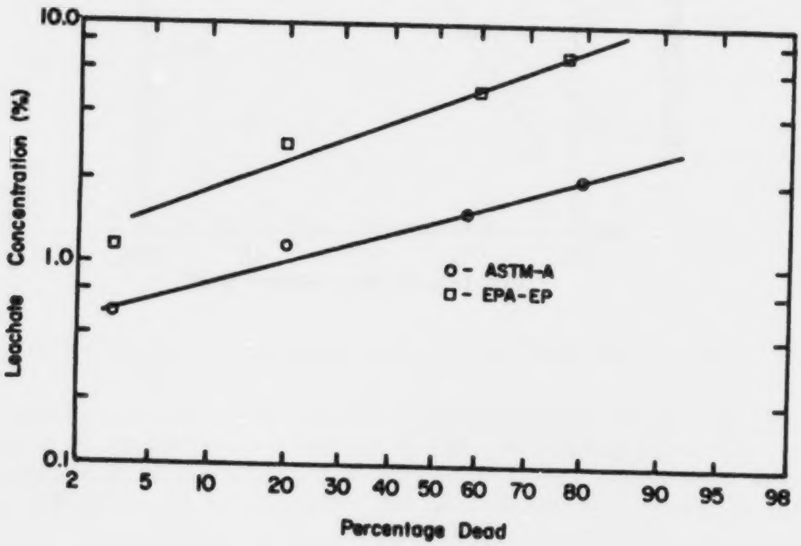

Figure 4. Daphnia Toxicity Data From Lime Sludge Leachates

CORRELATION OF DAPHNIA TOXICITY DATA WITH CHEMICAL COMPOSITION DATA

Biesinger (3) published Daphnia magna 48 hour LC-50 data for various primary and secondary EPA drinking water metals. Figure 5 is our plot of Biesinger's data illustrating that an empirical relationship exists for most heavy metals with EPA drinking water standards. It should be noted that drinking water standards are not based upon Daphnia magna toxicity data, and the correlation illustrated on figure 5 is quite emperical. The outlier points for copper and zinc represent the extreme toxicity of these metals to Daphnia magna, and lack of such toxicities to mammals and humans in specific.

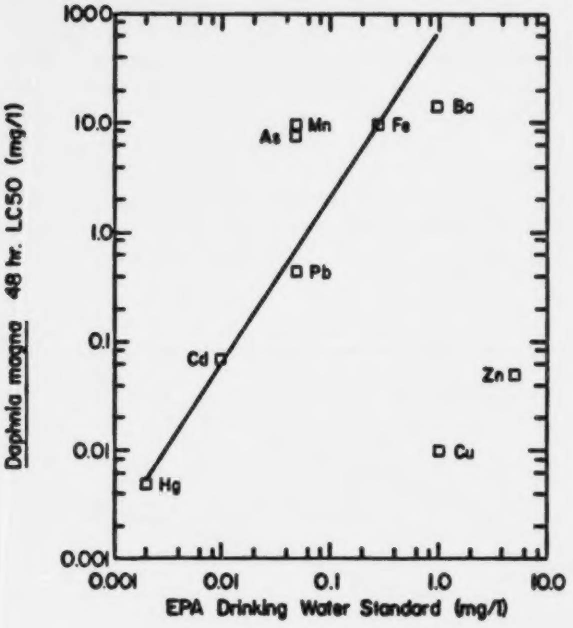

Figure 5. Correlation Between Daphnia Toxicity and Drinking Water Standards

In an attempt to correlate LC-50 data with metal characterization data of leachates, measured metal concentrations were weighted to account for the fact that some substances are more toxic to Daphnia magna than are other metals. The weighting procedure used was based upon the following equation:

$$\Sigma M = (Ca/Ca_o)+(Cd/Cd_o)+(Cu/Cu_o)+(Fe/Fe_o)+(Mg/Mg_o) +(Mn/Mn_o)+(Pb/Pb_o)+(Zn/Zn_o)$$

The numerator for each metal is the metal concentration for leachates as measured, and the denominator represents data published by Biesinger (3). The resultant equation, for application to data developed in this research is:

$$\Sigma M = (Ca/52)+(Cu/0.01)+(Fe/9.6)+(Mg/140) +(Mn/9.8)+(Zn/0.1)$$

Figure 6 is a correlation of Daphnia toxicity LC-50 values as measured in the course of this research with the measured weighted metal concentrations (ΣM) for leachates generated from coal conversion ash and slag residuals. The correlation with trace metals did not hold for wastewater treatment plant sludges, however, as shown on figure 7, LC-50 values for Daphnia toxicity are correlated with phenol concentrations measured in the ASTM-A and EPA "EP" leaching protocols of generated lime and alum wastewater treatment sludges.

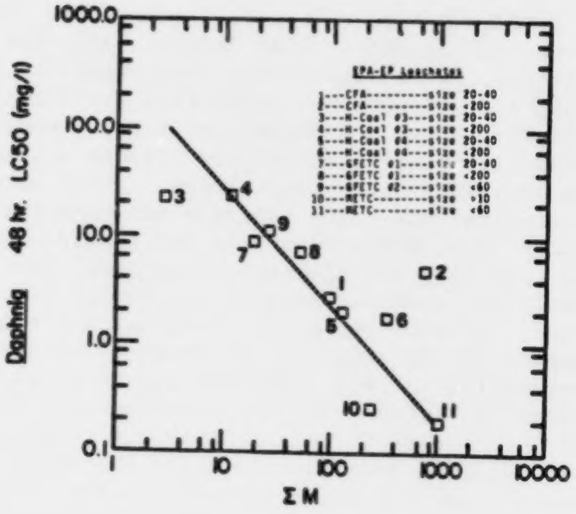

Figure 6. Relationship Between Daphnia Toxicity and Weighted Metal Concentrations of Ash and Bottom Leachates

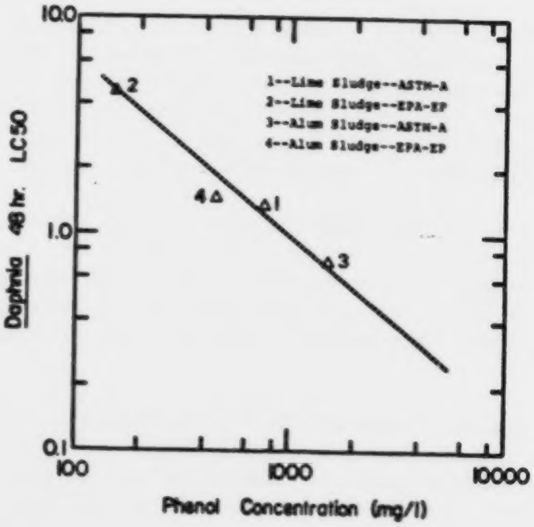

Figure 7. Relationship Between Daphnia LC50 Data and Phenol Concentration of Sludge Leachates

AMES TESTING FOR MUTAGENICITY POTENTIALS

SRC-II solid wastes generated at the Ft. Lewis pilot plant were provided by the Pittsburgh and Midway Coal Company under the guidance of the U.S. Department of Energy, Pittsburgh Energy Technology Center. The samples received were two shipments of vacuum bottoms from the vacuum flash drum of the direct liquefaction step, and wastewater sludges consisting of alum sludge from the pre-biological (flotation) step, waste activated biological sludge, and digested activated biological sludge. These samples were subjected to simple chemical screening analysis and Ames testing for potential mutagenicity. Both whole materials and liquid phases filtered from whole materials (for clarifier and digester biosludges) were evaluated for mutagenicity. In addition, a serial organic extraction protocol was developed using hexane, toluene, methylene chloride, and acetonitrile to gain a qualitative assessment of the polarity and chemical nature of leached substance causing mutagenicity. For clarifier and digester biosludges, both liquid and solid phases of filtered sludges were analyzed for Ames mutagenicity. It is interesting to note that in all cases, the filtrate of sludge samples showed negative Ames results while the whole sample and retained filtered solid samples showed positive results. Samples of the dried sludge were processed by sequential organic extraction as outlined above to generate four additional extracts and residue for testing. Five tester strains, TA98, TA100, TA1535, TA1537 and TA1538 were employed in the tests with and without microsomal activation. Routine sterility and toxicity checks were made during the course of the run. It was found that none of the mutagenicity tests which used TA1535 without S9 and TA1537 with S9 resulted in positive plates in early phases of the investigation, therefore, TA1535 was eliminated from all tests and TA1537 were not used when microsomal activation was applied.

The standard criteria used to define a positive result in the Ames bioassay for mutagenic activity include (a), a two-fold or greater increase in the number of revertants exposed to the test material compared to respontaneous revertant rates; (b), repeatability i.e...a confirmation of the positive result by running the test again after a two week period; (c), for compounds of low mutagenicity, a reproducible dose response rate.

Ames test results were uniformly negative where microsomal activation was not included in the test procedures. The most sensitive tester strain showing the greatest number of revertants compared to the spontaneous revertant rate is shown to be strain TA98 with S9, a result which agrees with other investigations. All other tester strains showed marginal positive results.

Toxicity to the tester organisms by test materials was encountered in all of the individual bioassays with alum sludges showing perhaps the highest toxicity. It is hypothesized that this may be due to either organics, or to the fine alum "slime" particles which interfered with growth of revertants.

The highest mutagenicity activity observed (revertants per mg) were exhibited by the vacuum bottoms solid wastes. Vacuum bottoms solid wastes contain organics that are not highly water soluble and thus the probability of release in a landfill is small. Clearly, mutagenic substances exist on these solid waste residuals as evidenced by conducting Ames testing of whole materials dissolved in organic solvents, but aqueous leachates show no mutagenic activity. Philosophical questions are raised leading to a need for policy delineation by EPA as to the acceptability of disposing of such materials in hazardous or conventional waste landfills.

Table 6 is a summary of Ames test results using tester strains TA98 with S9 activation. It should be noted that the average number of revertants for the control is 46 with standard deviation of 16. This table shows the whole vacuum bottoms residual gave rise to 13.2 times the number of revertants on a negative control plate (spontaneous revertants) for sample number 1936, while for vacuum bottoms sample number 2277 (sample numbers provided by the Pittsburgh and Midway Coal Mining Company), a ratio of 21.4 times spontaneous revertants were observed. As can be seen from this table, from a column of data using whole substances, the vacuum bottoms from the SRC-II Ft. Lewis facility show far more mutagenicity than do the other solid residuals measured. All solid residuals, as observed from the Ft. Lewis facility, give rise to positive mutagenicity potentials as determined by criteria of values being greater than 2 times the spontaneous revertants indicating positive Ames tests.

TABLE 6. AMES TESTING OF SRC-II FORT LEWIS SOLID WASTE RESIDUALS AND EXTRACT FRACTIONS

				ORGANIC SOLVENT EXTRACT FRACTIONS									
TEST SAMPLE	SAMPLE NUMBER	WHOLE*		HEXANE		TOLUENE		METHYLENE CHLORIDE		ACETONITRILE		RESIDUE	
		rev/mg	(R)	rev/mg	(R)	rev/mg	(R)	rev/mg	(R)	rev/mg	(R)	rev/mg	(R)
VACUUM BOTTOMS	1936	2875	13.2	11600	16.6	3695	39.4	2365	13.6	20330	25.5	560	2.5
	2277	11095	21.4	2567	15.6	12200	44.0	5552	13.8	9578	19.9	NM	2.0
ALUM SLUDGE	2280	7705	3.0	NM	NM	NM	NM	1987	5.1	1295	4.5	NM	NM
CLARIFIER SLUDGE	1937	4050	5.8	1268	3.9	1290	3.9	1349	5.0	14720	31.0	NM	NM
	2278	932	3.8	NM	NM	NM	NM	960	2.4	NM	NM	NM	NM
DIGESTER SLUDGE	1938	530	6.2	236	2.6	984	2.8	NM	NM	NM	NM	NM	NM
	2279	1273	2.8	NM	NM	2803	2.4	868	2.5	NM	NM	247	2.5

NOTE:

* "Specific Mutagenic Activity" for Vacuum Bottoms in revertants/mg for all other whole materials (sludges) in revertants/ml.

NM Not Mutagenic

R Ratio of revertants on test plate (spontaneous + induced)/spontaneous revertants on control plate

Work is continuing at the University of Pittsburgh in the area of evaluating mutagenicity potentials of wastewater sludges and their leachates when treating GFETC wastewaters, and the evaluations of methodologies of changing the pretreatment and biological treatment step to minimize such mutagenicity and toxicity potentials.

RESEARCH IN COMPUTER MODELING OF LEACHATE CONCENTRATIONS AT LANDFILL BOUNDARIES

A series of five simultaneous differential equations utilizing concepts of diffusivity, film diffusion, intraparticle diffusion and liquid-solid equilibria has been developed for the prediction of leachate compositions at the boundary line from a landfill containing coal gasification solid waste residuals. The model is based upon deterministic concepts and simple equilibrium and diffusion data and was calibrated in the lab using GFETC #1 slag residuals. The system of simultaneous differential equation has been solved using numerical computational methods.

This model has been extrapolated from lab scale to predict concentration profiles of a commercial scale landfill (600 meters x 600 meters x 6 meters deep) filled with coal conversion solid wastes. Under the assumption of unidirectional flows and small fluid velocity, profiles of concentration with duration at the landfill boundary were computed. As an example of the results of computer modeling, figure 8 is a plot of predicted concentration in leachates versus time for a coal conversion solid waste landfill where particle sizes are in range of 20 to 40 mesh at flooded conditions with indicated groundwater velocities through the landfill site.

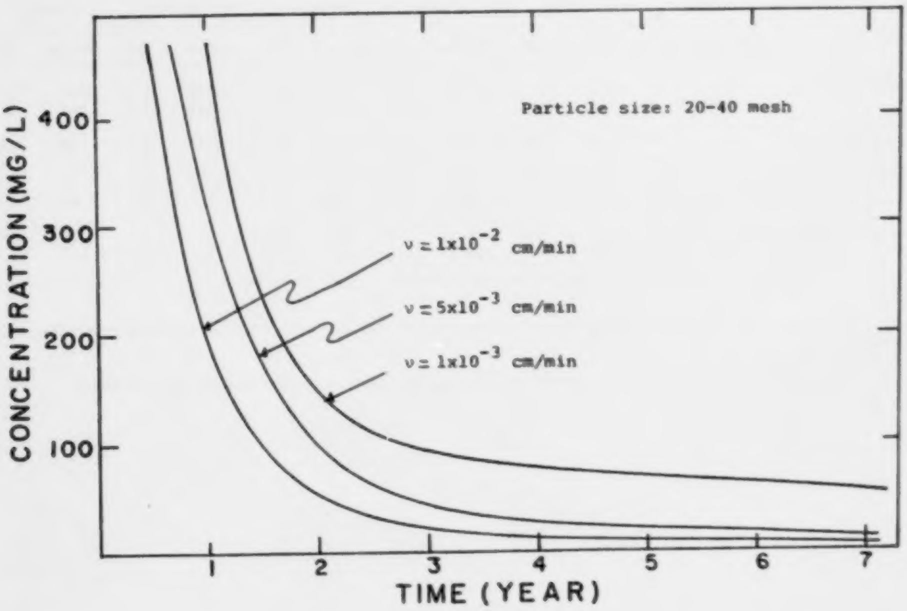

Figure 8. Calculated Calcium Concentration Profiles for a Landfill

By understanding the concepts and implications of intraparticle diffusion, figure 9 was developed for conditions of discontinuous flow. The breaks in the curve indicate periods of "no rain" or dry conditions. This figure illustrates the concept of "a first flush phenomena" by showing that under flooded conditions, steady state mass transfer from the solid phase to the liquid phase occurs, and is predictable. Under dry conditions, however, concentration of leachable pollutants at the particle surface increases with time to become uniform throughout due to intraparticle diffusion. The first flush phenomena, as shown on figure 9, predicts an increase in aqueous concentration over that which would be ordinarily expected under the flooding conditions shown in figure 8. The overall area under all the curves of figure 9 is proportional to the total quantity of leachable substances produced. As can be seen, commensing of flooding causes high excursions in aqueous concentration; this concept we call a "first flush phenomena". This model may predict difficulties in compliance with concentration restrictions as outlined by RCRA regulations for ash/slag landfills under conditions of "first flush" or discontinuous flows. Additional details are available in a dissertation by Erdogan (4).

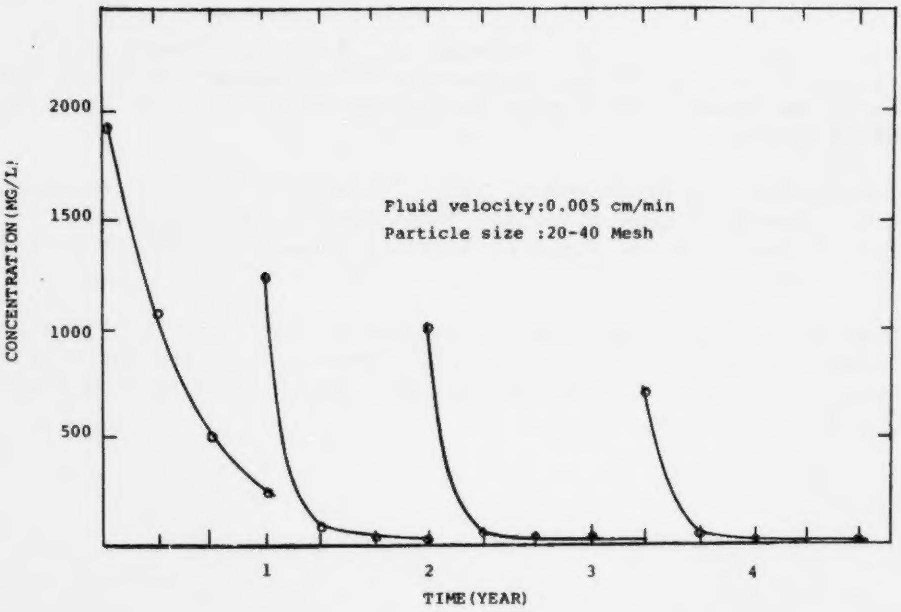

Figure 9. Predicted Concentration Profile for a Landfill with Discontinuous Flow

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UPDATE ON EPA'S REGULATORY VIEWS ON COAL CONVERSION SOLID WASTES†

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ABSTRACT

The Resource Conservation and Recovery Act of 1976 (RCRA) charges EPA with the responsibility for establishing a program for the management of hazardous solid wastes. This paper summarizes current and anticipated RCRA regulations affecting the synfuels industry. Included in the various RCRA issues pertaining to the synfuels industry is a discussion of the RCRA mining exemption. An overview is given of the Office of Solid Waste's planned research activities to support future synfuels solid waste regulations.

(Only the abstract is published herein.)

Session V: MULTIMEDIA ENVIRONMENTAL CONSIDERATIONS

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Cochairman: John T. Dale
U.S. Environmental Protection Agency, Region VIII
Denver, CO

A PERMITTER'S VIEW OF SYNFUEL COMMERCIALIZATION[†]

by: George L. Harlow
Air and Hazardous Materials Division
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Region IV
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ABSTRACT

The Environmental Protection Agency has responsibility for the issuance of permits to synfuel plants for the control of various liquid, gaseous, and solid waste streams. These permits comprise the Prevention of Significant Deterioration (PSD) under the Clean Air Act of 1977, the National Pollutant Discharge Elimination System (NPDES) and the Section 404 Dredge and Fill permits under the Clean Water Act of 1977 and the hazardous waste permits under the Resource Conservation and Recovery Act (RCRA) of 1976.

Since there will likely not be federal regulations established by EPA setting standards on requirements for the first generation synfuel plants, the environmental permits will have to be individually negotiated, case by case, with each applicant using best engineering practice. This places an unusual burden upon the permit writer who will be negotiating with the discharger from an uninformed and defenseless position. In order to overcome this burden and to avoid long, time-consuming delays in the permit process, the company should disclose in its application for permit exactly what steps will be taken to control air emissions, water discharges and hazardous wastes.

(Only the abstract is published herein.)

PB83-128413

COMPARISON OF ENVIRONMENTAL DESIGN ASPECTS OF SOME LURGI-BASED SYNFUELS PLANTS †

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INTRODUCTION

A number of commercial-scale projects have been proposed in the United States for the production of gas and liquid synfuels from coal. Many of these proposed projects are planning to use Lurgi coal gasifiers and related Lurgi technology such as the Rectisol gas purification process and the Phenosolvan process for recovering phenols from coal gasification wastewaters. These projects represent several different architectural and engineering contractors and, therefore, probably different design philosophies and preferences. As a result, a comparison of how each contractor handled some of the environmental concerns would indicate a segment of industry's views on plant configurations and control alternatives.

Table 1 identifies 14 Lurgi-based synfuels projects which are currently being proposed, studied, or underway in the United States. In terms of their design progress, their environmental permitting status, and their investment financing arrangements, the most advanced project among those listed in Table 1 appears to be the Great Plains Gasification Associates' project in North Dakota. Some of the other projects have completed fairly detailed feasibility studies and have prepared environmental impact studies as well as environmental permitting applications. However, none of the other projects appear to be as well advanced as the Great Plains project in North Dakota.

Process design information has been obtained for five of the projects listed in Table 1[1-9], and this paper describes and compares the key environmental design aspects and features of these five projects:

- The Great Plains Gasification Associates' project in North Dakota (initiated by the American Natural Gas Service Company).
- The Hampshire Energy Company's project in Wyoming.
- The Nokota Company's project in North Dakota (initiated by the Natural Gas Pipeline Company of America).
- The Tenneco project in Montana (known as the Beach-Wibaux project).
- The WyCoalGas, Inc. project in Wyoming (a subsidiary of Panhandle Eastern Pipe Line Company).

TABLE 1. PROPOSED COAL GASIFICATION PROJECTS PLANNING TO USE LURGI GASIFIERS

PROJECT SPONSOR	LOCATION	TYPE OF GASIFIERS	TOTAL COAL, T/D (Mg/D)	A&E CONTRACTOR	PRIMARY PRODUCTS
Tri-State Synfuels	Kentucky	Lurgi	28,000 (25,400)	Fluor	High-Btu SNG, gasoline, and chemicals
Louisiana Gasification Associates	Louisiana	Lurgi	n.a.	n.a.	Synthesis gas
Crow Indians	Montana	Lurgi	12,000 (10,900)	Fluor	High-Btu SNG
Tenneco Coal Gasification	Montana	Lurgi	41,000 (37,200)	Fluor	High-Btu SNG
Texas Eastern Synfuels	New Mexico	Lurgi	30,000 (27,200)	Bechtel	High-Btu SNG and methanol
Great Plains Gasification Associates	N. Dakota	Lurgi	28,700 (26,000) [b]	Lummus	High-Btu SNG
Nokota Company	N. Dakota	Lurgi	42,000 (38,100)	Fluor	High-Btu SNG and methanol
North Dakota Synfuels Group	N. Dakota	Lurgi	20,000 (18,100)	Stone & Webster	High-Btu SNG and methanol
Exxon USA	Texas	Lurgi	42,000 (38,100)	n.a.	Synthesis gas
Transco Energy Company	Texas	Lurgi	n.a.	n.a.	Medium-Btu gas
Ohio Valley Synthetic Fuels	W. Virginia	BGC/Lurgi [c] and Texaco	50,000 (45,400) [d]	Foster Wheeler	High-Btu SNG and methanol
Hampshire Energy Company	Wyoming	Lurgi and KBW [a]	15,000 (13,600)	Fluor	Gasoline, propane, and butanes
Lake Desmet Synfuels	Wyoming	Lurgi	38,000 (34,500)	n.a.	High-Btu SNG and methanol
WyCoalGas, Inc	Wyoming	Lurgi	32,600 (29,600)	Bechtel	High-Btu SNG

[a] Koppers and Babcock-Wilcox entrained gasifiers.

[b] To be built in 2 phases, each for 14,350 T/D (13,000 Mg/D) of coal.

[c] British Gas Corporation and Lurgi slagging gasifiers.

[d] To be built in 3 phases: phase 1 = 5,000 T/D (4500 Mg/D) coal, phase 2 = 25,000 T/D (22,700 Mg/D) coal, phase 3 = 50,000 T/D (45,400 Mg/D).

n.a. Not available, or not yet selected

The gasifier feedstock coals for the five projects are summarized below, on a "run-of-mine" basis:

PROJECT	COAL RANK	AMOUNT T/D (Mg/D)	HEATING VALUE, Btu/lb (kJ/kg)	SULFUR % Wt
Great Plains	Lignite	28,670 (26,000)	7,185 (16,710)	1.01
Hampshire	Subbituminous	15,000 (13,600)	8,075 (18,780)	0.33
Nokota	Lignite	28,350 (25,700)	6,985 (16,250)	0.85
Tenneco	Lignite	33,000 (29,900)	7,020 (16,330)	0.82
WyCoalGas	Subbituminous	22,820 (20,700)	8,450 (19,650)	0.32

These coal amounts refer specifically to the gasifier feedstock coal, whereas the amounts given in Table 1 include any coal burned in boilers to generate plant steam as well as any coal fines returned to the mine or sent elsewhere.

OVERALL PROCESS DESIGNS

The five coal-to-synfuels plant designs described in this paper use a number of individual process steps, arranged in various configurations. The major process steps are briefly described below:

Lurgi gasification — Coal, steam, and oxygen are reacted and result in a crude gas containing hydrogen, carbon monoxide, carbon dioxide, methane, excess steam, hydrogen sulfide, ammonia, and various byproducts and impurities. The crude gas is washed and cooled, condensing out a "gas liquor" containing water, tars, oil, phenols, and ammonia.

Shift conversion — Part of the carbon monoxide in the crude gas is "shifted" (i.e., converted to carbon dioxide and hydrogen), so as to provide the ratio of hydrogen to carbon monoxide needed for the subsequent synthesis of methanol or methane. The shifted gas is then further cooled, condensing out additional gas liquor.

Gas purification – The acid gases hydrogen sulfide and carbon dioxide are removed from the shifted gas by absorption in a solvent, using the Rectisol process and, in one case, the Selexol process. The shifted and purified gas is then routed to the subsequent synthesis step to produce either methanol or methane. The absorbed gases are stripped from the absorption solvent and recovered as acid gas streams. Those which are rich in hydrogen sulfide are processed further for conversion into sulfur.

Methanol synthesis – The hydrogen and carbon monoxide in the purified gas are reacted in the presence of a specific synthesis catalyst to form methanol. The methanol synthesis step also generates a purge gas stream, which may be further processed for conversion into methane and/or to provide a source of hydrogen for hydrotreating of Lurgi byproduct naphtha. The methanol produced may be sold as a product or may be processed further for conversion into gasoline.

Methanation – The hydrogen and carbon monoxide in the purified gas (from shift conversion and gas purification), or in the methanol synthesis purge gas, are reacted in the presence of a specific methanation catalyst to form methane. Methane is the principal constituent of the product SNG (substitute natural gas).

Gas liquor cleanup – Tars and oils are separated from the gas liquor and recovered. Next, the bulk of the phenols in the gas liquor are removed by the Phenosolvan process[10], which uses extraction by a selective solvent. Ammonia is then stripped from the dephenolized gas liquor and recovered as a byproduct. The further treatment of the residual wastewater (stripped and dephenolized gas liquor) is described later in this paper.

Partial oxidation – Liquid hydrocarbon byproducts (such as the Lurgi tars, oils, naphtha, and phenols) may be reacted with steam and oxygen to result in a crude gas containing hydrogen, carbon monoxide, carbon dioxide, excess steam, hydrogen sulfide, ammonia, and a very small amount of methane and other impurities. The subsequent processing of the partial oxidation crude gas is very similar to that described herein for the Lurgi crude gas.

Gasoline production – The MTG (methanol to gasoline) process first catalytically converts methanol to a mixture of methanol, dimethyl ether, and water vapor. The methanol and dimethyl ether are then catalytically converted to form hydrocarbons in the gasoline boiling range (C_4 to C_{10}). The hydrocarbons are fractionated into stabilized gasoline, LPG, and butanes. Part of the butanes are alkylated to form additional high-octane gasoline. The Lurgi naphtha is desulfurized in a catalytic hydrotreater to provide an additional gasoline component. Thus, the product gasoline includes stabilized MTG gasoline, alkylate, and hydrotreated Lurgi naphtha.

KBW gasification – Lurgi gasifiers require a sized coal in the range of 0.25 – 1.50 in. (0.64 – 3.8 cm). Thus, the coal fines produced from crushing and sizing of run-of-mine coal could be used as boiler fuel, disposed of in the mine or elsewhere, or gasified in some other type of gasifier. Entrained bed gasifiers, such as the KBW gasifiers (see Table 1), may be used to react the coal fines with steam and oxygen to produce a crude gas containing hydrogen, carbon monoxide, carbon dioxide, excess steam, hydrogen sulfide, ammonia, and a very small amount of methane and other impurities. The subsequent processing of the crude gas is very similar to that described herein for the Lurgi crude gas.

Sulfur recovery – It is beyond the scope of this paper to describe the many different processes that could be used for converting hydrogen-sulfide-rich acid gases into recovered sulfur. However, since four of the five coal-to-synfuels plant designs discussed in this paper plan to use the Stretford process, that process is described briefly herein.

The Stretford process involves liquid-phase oxidation of hydrogen sulfide in an aqueous solution of sodium vanadate and anthraquinone disulfonic acid (ADA). The hydrogen sulfide is absorbed and oxidized to sulfur, which is subsequently removed as a froth by flotation and purified by centrifuging followed by melting. The Stretford process can be designed to remove essentially all of the hydrogen sulfide in the feedstock gas and convert it into byproduct sulfur. However, the Stretford process accomplishes little, if any, removal and conversion of organic sulfur compounds such as carbonyl sulfide (COS), carbon disulfide (CS_2), and mercaptans (RSH), all of which are present in varying amounts in the gasification crude gases.

The flow diagram in Figure 1 presents the overall process design for the Hampshire project. Some key points of this design are:

- The products and byproducts are gasoline, LPG, butanes, sulfur, ammonia, and carbon dioxide.
- Coal fines are gasified in KBW gasifiers, eliminating the need to burn any coal fines.
- Plant steam and power are supplied by burning methanol synthesis purge gas in gas turbines and generating steam by recovering heat from the turbine exhaust flue gases.
- Lurgi byproduct tars, oils, and phenols are gasified via partial oxidation.
- The combined Lurgi, KBW, and partial oxidation crude gases are purified in a selective Rectisol unit.
- Sulfur recovery utilizes the Adip, Claus, and Scot processes.

The flow diagram in Figure 2 presents the overall process design for the Tenneco project. Some key points of this design are:

- The products and byproducts are SNG, sulfur, and ammonia.
- Coal fines are burned in steam-generating boilers. Electrostatic precipitators (ESPs) followed by wet limestone scrubbers provide flue gas particulate removal and flue gas desulfurization.
- Lurgi tars, oils, naphtha, and phenols are gasified via partial oxidation.
- The Lurgi crude gas is purified in a non-selective Rectisol unit, and the partial oxidation crude gas is purified in a selective Selexol unit.
- Sulfur recovery utilizes the Stretford process.

The flow diagram in Figure 3 presents the overall process design for the Nokota project. Some key points of this design are:

- The products and byproducts are methanol, SNG, phenols, oil, naphtha, sulfur, and ammonia. Excess coal fines will be either a byproduct or waste.
- Coal fines and Lurgi tars are burned in steam-generating boilers. Dry scrubbing followed by baghouses provide flue gas desulfurization and flue gas particulate removal.
- The Lurgi crude gas is purified in a selective Rectisol unit.
- Sulfur recovery utilizes the Stretford process.

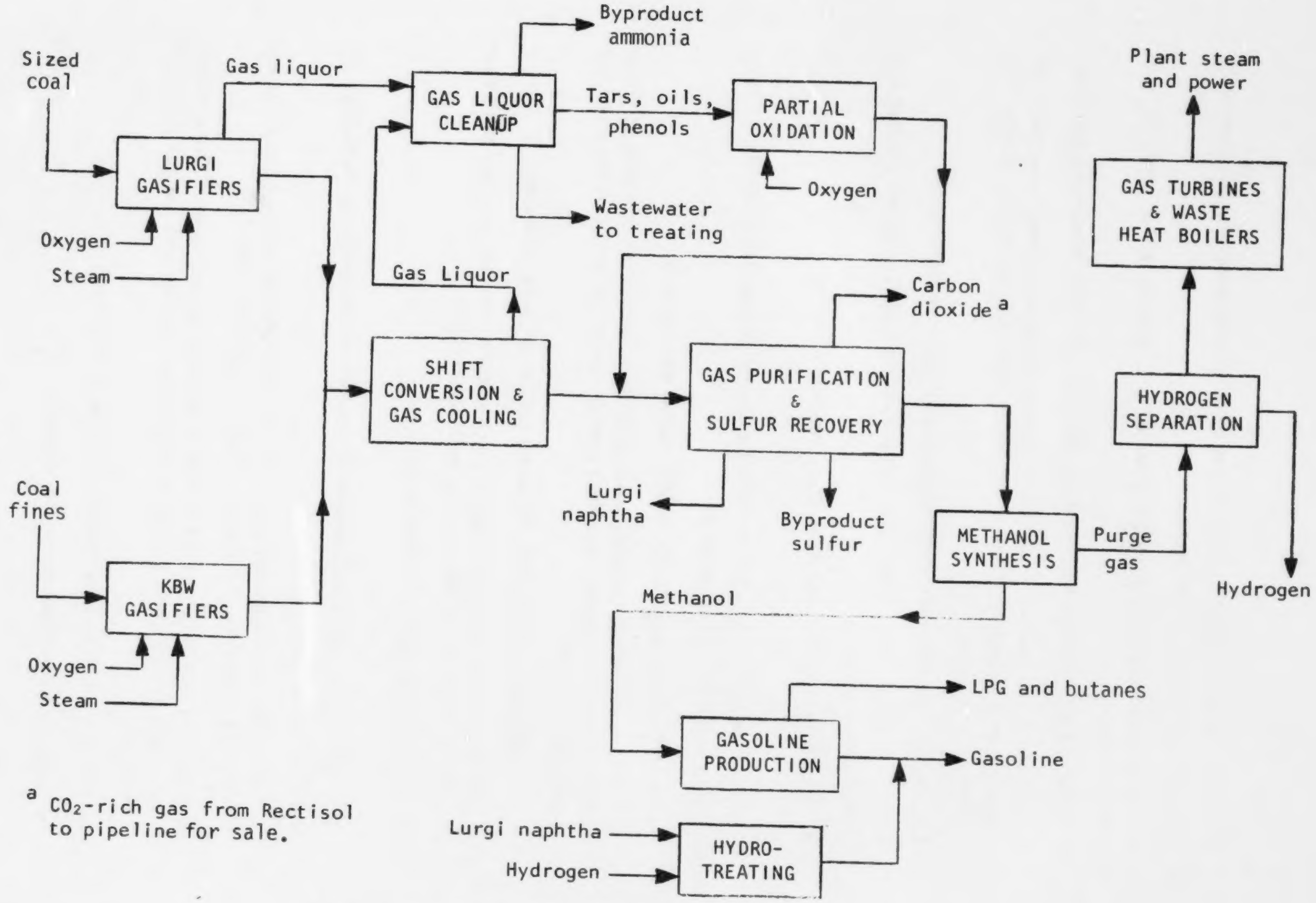
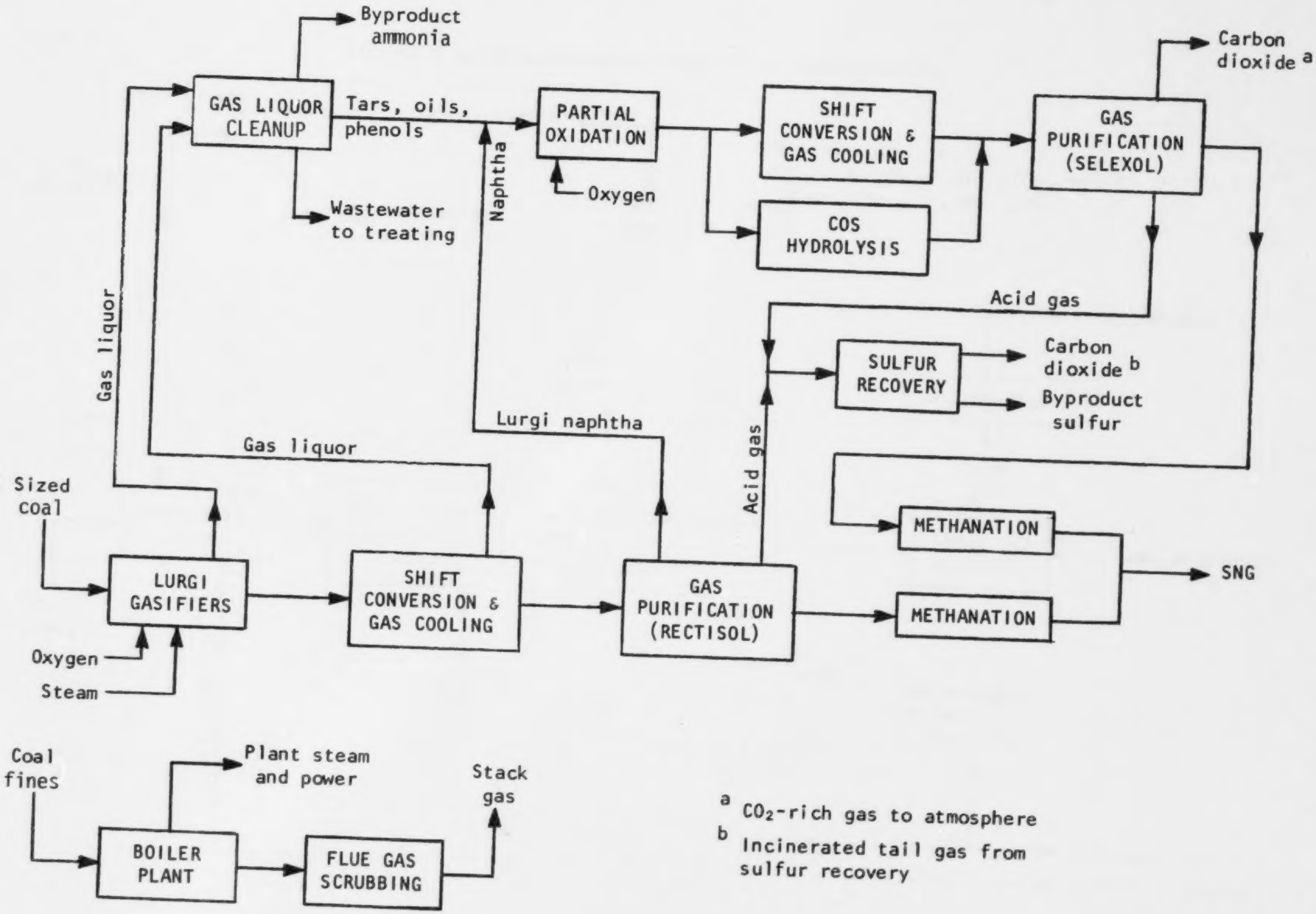

Sized coal
LURGI GASIFIERS
Oxygen
Steam
Gas liquor
GAS LIQUOR CLEANUP
Byproduct ammonia
Tars, oils, phenols
Wastewater to treating
PARTIAL OXIDATION
Oxygen
Gas Liquor
SHIFT CONVERSION & GAS COOLING
GAS PURIFICATION & SULFUR RECOVERY
Carbon dioxide a
Lurgi naphtha
Byproduct sulfur
METHANOL SYNTHESIS
Purge gas
HYDROGEN SEPARATION
Hydrogen
GAS TURBINES & WASTE HEAT BOILERS
Plant steam and power
Coal fines
KBW GASIFIERS
Oxygen
Steam
Methanol
GASOLINE PRODUCTION
LPG and butanes
Gasoline
Lurgi naphtha
Hydrogen
HYDRO-TREATING

FIGURE 1. HAMPSHIRE ENERGY COMPANY (WYOMING) PROJECT

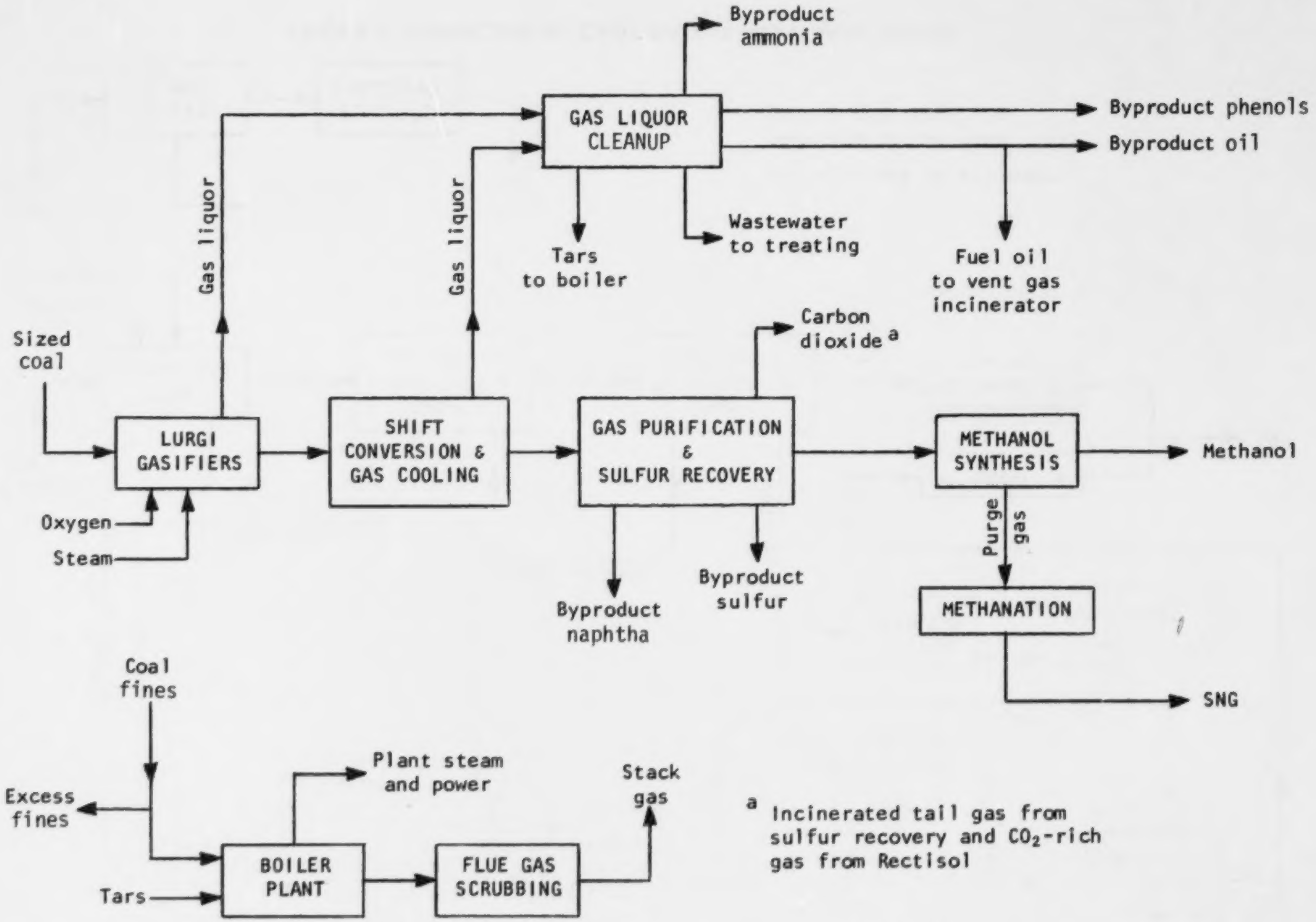
[a] CO_2-rich gas from Rectisol to pipeline for sale.


Byproduct ammonia
GAS LIQUOR CLEANUP
Tars, oils, phenols
Wastewater to treating
Naphtha
PARTIAL OXIDATION
Oxygen
SHIFT CONVERSION & GAS COOLING
COS HYDROLYSIS
GAS PURIFICATION (SELEXOL)
Carbon dioxide a
Acid gas
SULFUR RECOVERY
Carbon dioxide b
Byproduct sulfur
Gas liquor
Gas liquor
Lurgi naphtha
Acid gas
Sized coal
LURGI GASIFIERS
Oxygen
Steam
SHIFT CONVERSION & GAS COOLING
GAS PURIFICATION (RECTISOL)
METHANATION
METHANATION
SNG
Coal fines
BOILER PLANT
Plant steam and power
FLUE GAS SCRUBBING
Stack gas

[a] CO_2-rich gas to atmosphere

[b] Incinerated tail gas from sulfur recovery

FIGURE 2. TENNECO COAL GASIFICATION (MONTANA) PROJECT


Byproduct ammonia
GAS LIQUOR CLEANUP
Byproduct phenols
Byproduct oil
Gas liquor
Gas liquor
Tars to boiler
Wastewater to treating
Fuel oil to vent gas incinerator
Carbon dioxide a
Sized coal
LURGI GASIFIERS
SHIFT CONVERSION & GAS COOLING
GAS PURIFICATION & SULFUR RECOVERY
METHANOL SYNTHESIS
Methanol
Oxygen
Steam
Purge gas
Byproduct naphtha
Byproduct sulfur
METHANATION
SNG
Coal fines
Plant steam and power
Stack gas
Excess fines
BOILER PLANT
FLUE GAS SCRUBBING
Tars

[a] Incinerated tail gas from sulfur recovery and CO_2-rich gas from Rectisol

FIGURE 3. NOKOTA COMPANY (NORTH DAKOTA) PROJECT

The flow diagram in Figure 4 presents the overall process design for the WyCoalGas project. Some key points of this design are:

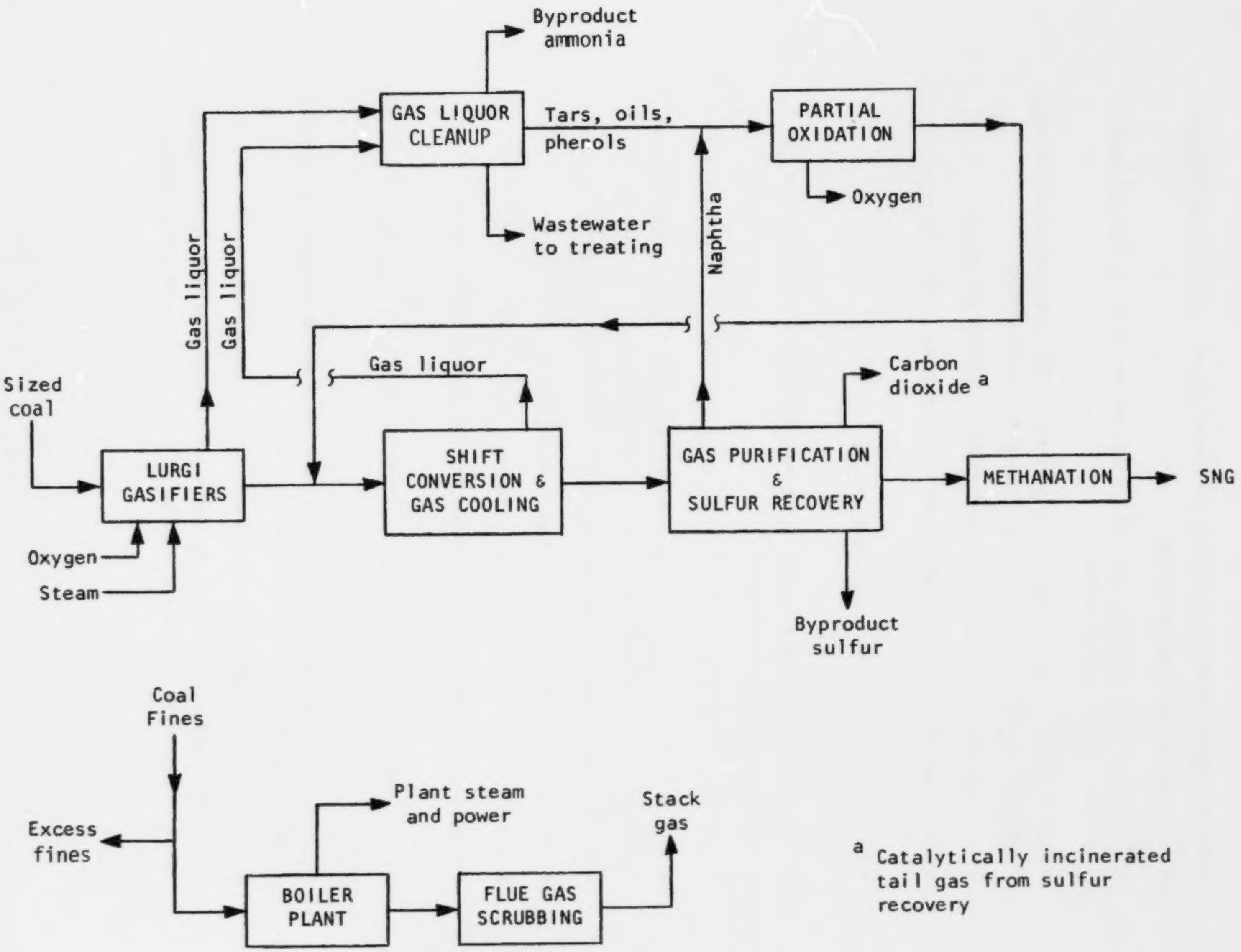
- The products and byproducts are SNG, sulfur, and ammonia. Excess coal fines will be either a byproduct or a waste.
- Coal fines are burned in steam-generating boilers. ESPs followed by wet limestone scrubbers provide flue gas particulate removal and desulfurization.
- Lurgi tars, oils, naphtha, and phenols are gasified via partial oxidation.
- The combined Lurgi and partial oxidation crude gases are purified in a non-selective Rectisol unit.
- Sulfur recovery utilizes the Stretford process.

The flow diagram in Figure 5 presents the overall process design for the Great Plains project. Some key points of this design are:

- The products and byproducts are SNG, sulfur, ammonia, and all of the coal fines.
- Lurgi tars, oils, naphtha, and phenols are burned as fuel in steam generating boilers. Particulates are removed from the tar-fired superheater's flue gas by an ESP.
- Lurgi naphtha and phenols are also burned as fuel in wastewater incinerator.
- The Lurgi crude gas is purified in a non-selective Rectisol unit.
- Sulfur recovery utilizes the Stretford process.
- A small amount of methanol is produced for Rectisol absorbent makeup.

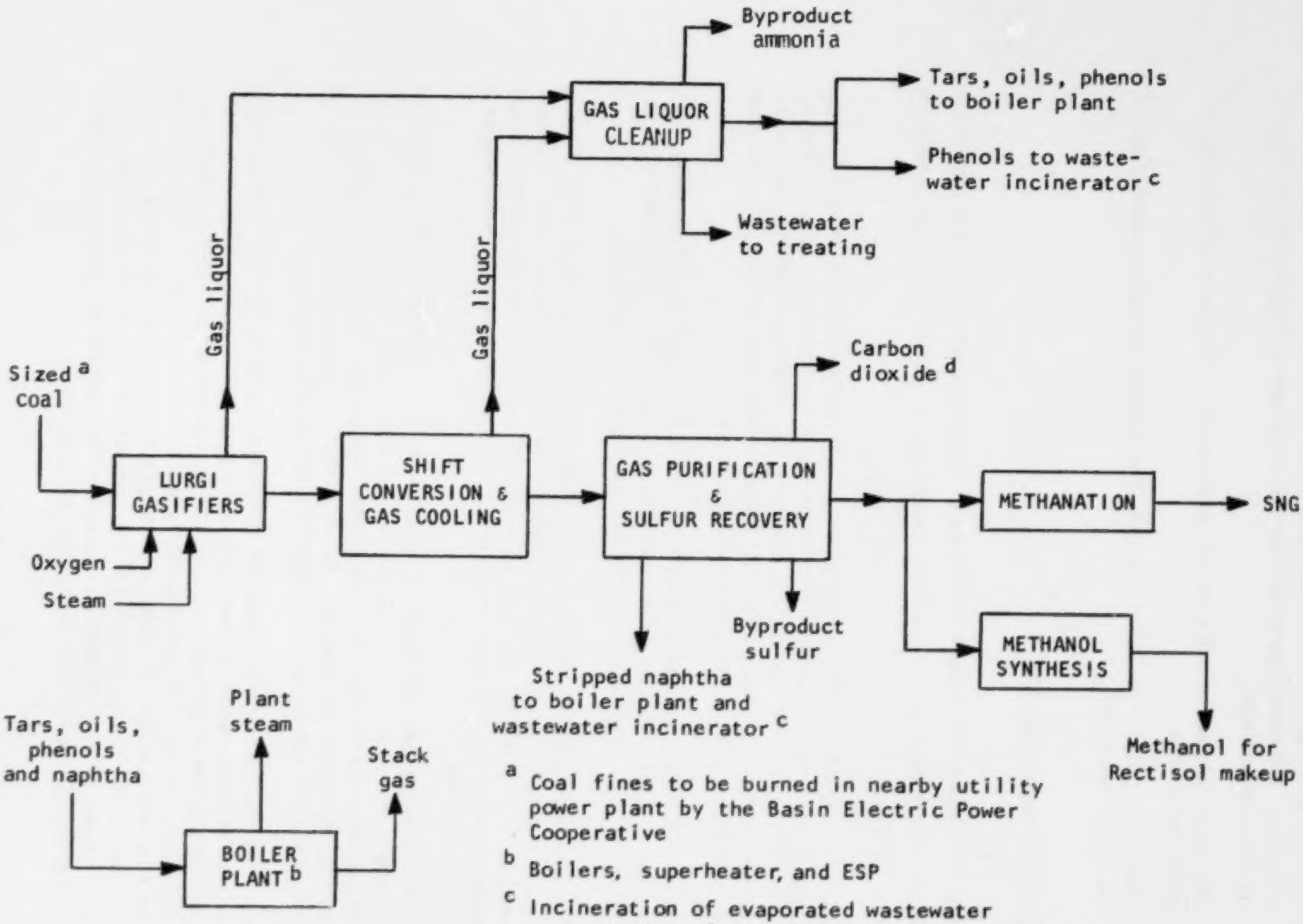
As an overall commentary on the five plant designs, it is of interest to note the following:

- Three of the five designs use partial oxidation to gasify the Lurgi liquids (tars, oils, naphtha, and phenols) for on-site use.
- Four of the five designs utilize the Stretford sulfur recovery process.
- Two of the designs use selective Rectisol for acid gas removal, two use non-selective Rectisol, and one uses both a selective Selexol unit and a non-selective Rectisol unit.


Byproduct ammonia
GAS LIQUOR CLEANUP
Tars, oils, pherols
PARTIAL OXIDATION
Oxygen
Wastewater to treating
Naphtha
Gas liquor
Gas liquor
Sized coal
Gas liquor
Carbon dioxide a
LURGI GASIFIERS
SHIFT CONVERSION & GAS COOLING
GAS PURIFICATION & SULFUR RECOVERY
METHANATION
SNG
Oxygen
Steam
Byproduct sulfur
Coal Fines
Plant steam and power
Stack gas
Excess fines
BOILER PLANT
FLUE GAS SCRUBBING

[a] Catalytically incinerated tail gas from sulfur recovery

FIGURE 4. WYCOALGAS, INC. (WYOMING) PROJECT


Sized[a] coal
Oxygen
Steam
LURGI GASIFIERS
Gas liquor
SHIFT CONVERSION & GAS COOLING
Gas liquor
GAS LIQUOR CLEANUP
Byproduct ammonia
Tars, oils, phenols to boiler plant
Phenols to waste-water incinerator[c]
Wastewater to treating
GAS PURIFICATION & SULFUR RECOVERY
Carbon dioxide[d]
Byproduct sulfur
Stripped naphtha to boiler plant and wastewater incinerator[c]
METHANATION
SNG
METHANOL SYNTHESIS
Methanol for Rectisol makeup
Tars, oils, phenols and naphtha
BOILER PLANT[b]
Plant steam
Stack gas

[a] Coal fines to be burned in nearby utility power plant by the Basin Electric Power Cooperative

[b] Boilers, superheater, and ESP

[c] Incineration of evaporated wastewater concentrate using naphtha and phenols as fuel

[d] Incinerated tail gas from sulfur recovery

FIGURE 5. GREAT PLAINS GASIFICATION ASSOCIATES (NORTH DAKOTA) PROJECT

- All three of the designs which burn coal to generate steam include flue gas desulfurization. The one design which burns liquids to generate steam does not include flue gas desulfurization.
- One design gasifies the coal fines and generates steam and power by burning purge gas in gas turbines.
- There is a broad diversity of products, byproducts, and process configurations among the five designs.

SULFUR EMISSIONS CONTROL

Figure 6 presents flow diagrams of the sulfur emissions control systems in each of the five coal-to-synfuels designs. In examining these systems, certain process characteristics should be kept in mind:

> Selective acid gas removal processes (either Rectisol or Selexol) are those which produce (a) carbon-dioxide-rich offgas from which most of the hydrogen sulfide has been removed and (b) an acid gas stream (often called the hydrogen-sulfide-rich stream) which is also carbon-dioxide-rich but contains most of the hydrogen sulfide removed from the shifted, gasifier product crude gas.
>
> Non-selective acid gas removal processes (either Rectisol or Selexol) are those which produce a single acid gas stream containing all of the carbon dioxide and all of the hydrogen sulfide removed from the shifted, gasifier product crude gas.
>
> The carbon-dioxide-rich offgas and the acid gas streams, produced by either selective or non-selective Rectisol or Selexol processes, contain hydrocarbon gases. Independent of any sulfur emissions control considerations, the carbon-dioxide-rich offgas and acid gas streams could be controlled (e.g. by incineration), to reduce the emissions of hydrocarbons[11].
>
> The designs indicate that essentially all of the hydrogen sulfide fed to the Stretford process is converted into byproduct sulfur, but little (if any) organic sulfur is converted into byproduct sulfur. Thus, the residual tail gas from a Stretford process might be incinerated for two reasons: (a) to control the emissions of hydrocarbons as discussed above and (b) to convert organic sulfur to sulfur dioxide.
>
> An Adip unit concentrates a hydrogen-sulfide-containing acid gas by removing hydrocarbons and some carbon dioxide from the acid gas. About 94 – 98 percent of the hydrogen sulfide in the acid gas can then be converted into byproduct sulfur in a Claus unit. A Scot unit converts the residual sulfur compounds in a Claus unit tail gas into hydrogen sulfide, which is then recovered and recycled to the Claus unit. The only sulfur species remaining in the Scot unit tail gas in any potentially significant amount (200 – 500 ppmv) is hydrogen sulfide, and the tail gas is usually incinerated to convert the hydrogen sulfide into sulfur dioxide.

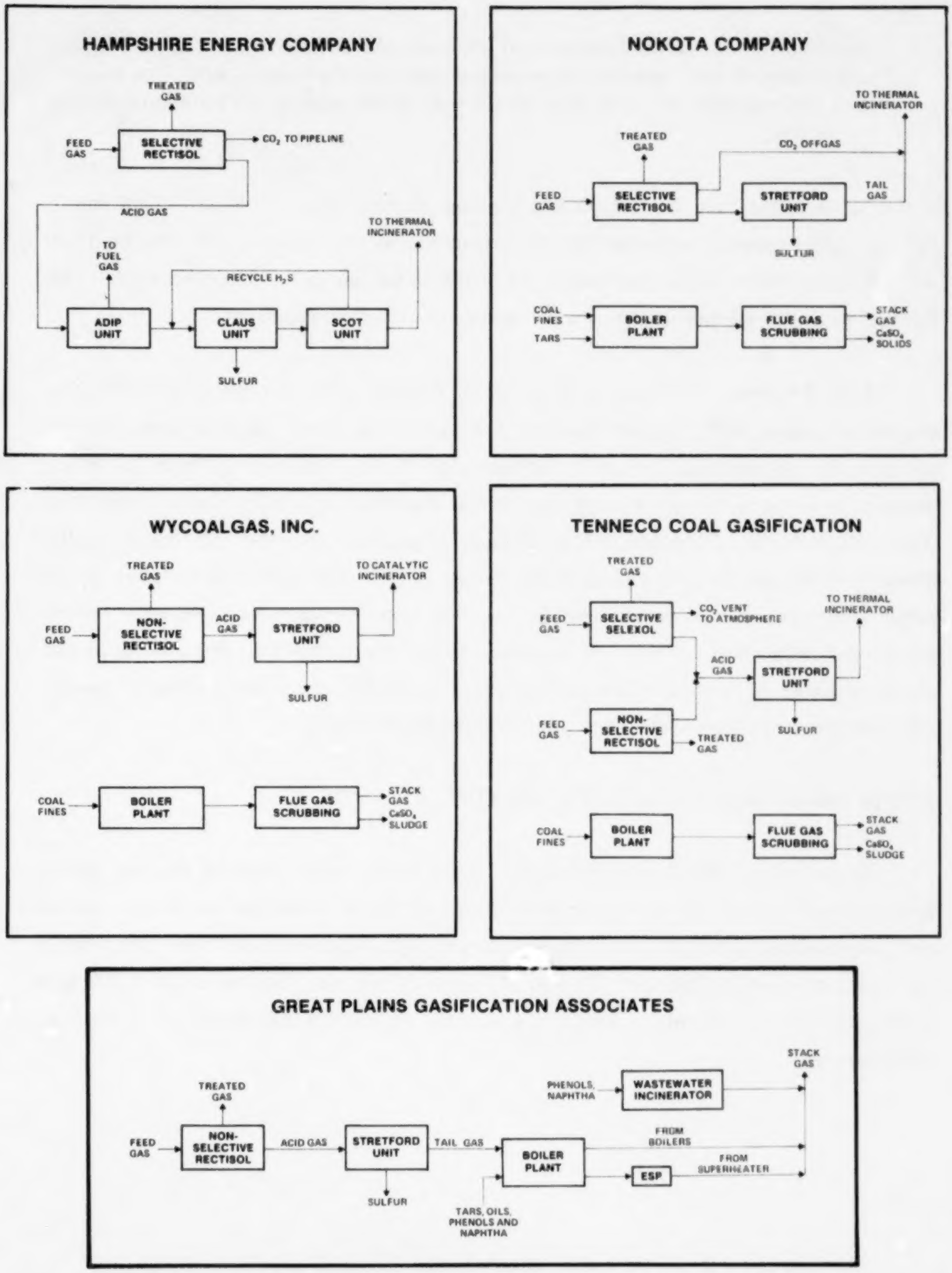

HAMPSHIRE ENERGY COMPANY
TREATED GAS
FEED GAS
SELECTIVE RECTISOL
CO₂ TO PIPELINE
ACID GAS
TO FUEL GAS
TO THERMAL INCINERATOR
RECYCLE H₂S
ADIP UNIT
CLAUS UNIT
SCOT UNIT
SULFUR
NOKOTA COMPANY
TO THERMAL INCINERATOR
TREATED GAS
CO₂ OFFGAS
FEED GAS
SELECTIVE RECTISOL
STRETFORD UNIT
TAIL GAS
SULFUR
COAL FINES
TARS
BOILER PLANT
FLUE GAS SCRUBBING
STACK GAS
CaSO₄ SOLIDS
WYCOALGAS, INC.
TREATED GAS
TO CATALYTIC INCINERATOR
FEED GAS
NON-SELECTIVE RECTISOL
ACID GAS
STRETFORD UNIT
SULFUR
COAL FINES
BOILER PLANT
FLUE GAS SCRUBBING
STACK GAS
CaSO₄ SLUDGE
TENNECO COAL GASIFICATION
TREATED GAS
FEED GAS
SELECTIVE SELEXOL
CO₂ VENT TO ATMOSPHERE
TO THERMAL INCINERATOR
ACID GAS
STRETFORD UNIT
FEED GAS
NON-SELECTIVE RECTISOL
TREATED GAS
SULFUR
COAL FINES
BOILER PLANT
FLUE GAS SCRUBBING
STACK GAS
CaSO₄ SLUDGE
GREAT PLAINS GASIFICATION ASSOCIATES
STACK GAS
PHENOLS, NAPHTHA
WASTEWATER INCINERATOR
TREATED GAS
FEED GAS
NON-SELECTIVE RECTISOL
ACID GAS
STRETFORD UNIT
TAIL GAS
BOILER PLANT
FROM BOILERS
FROM SUPERHEATER
ESP
SULFUR
TARS, OILS, PHENOLS AND NAPHTHA

FIGURE 6. SULFUR EMISSIONS CONTROL IN FIVE OF THE PROPOSED COAL GASIFICATION PROJECTS

Depressuring the coal lockhoppers on the Lurgi gasifiers, each time they are loaded with feedstock coal, requires the venting of gas from the lockhoppers. That gas contains hydrocarbons and acid gases, and it may be desirable to recover and/or incinerate the gas.

It should be noted that the Nokota and Tenneco designs incinerate Stretford tail gas in fuel-fired incinerators, the WyCoalGas design catalytically incinerates the Stretford tail gas, and the Great Plains design incinerates the Stretford tail gas in the boiler fireboxes. The Scot tail gas in the Hampshire design is incinerated in a gas-fired incinerator.

Table 2 summarizes the sulfur balances for the gasification process units for the five designs (excluding sulfur derived from any burning of coal fines). As a percentage of the sulfur in the gasified coal, the sulfur discharges for the five designs range from 2.8 to 5.3 percent. In terms of equivalent sulfur dioxide, the discharges for the five designs range from 0.02 to 0.15 lb per million Btu (8.6 to 65 ng/J) of gasified coal. Also note that the sulfur allocated to the gasifier ash in three of the designs ranges from about 3 to 7 percent of the sulfur in the gasified coal, which is within the usual range of assumption. However, one of the designs allocates 0.1 percent of the coal sulfur to the gasifier ash, and another of the designs allocates 13 percent of the coal sulfur to the gasifier ash. It is not known if special circumstances or data are available to support these assumptions.

WATER USAGE AND WASTEWATER TREATMENT

As shown in Table 3, the intake and usage of raw water ranges for the five coal-to-synfuels designs from 1.00 to 1.80 tons (1.00 to 1.80 Mg) of water per ton (Mg) of gasified coal, and the average is 1.26 tons (1.26 Mg) per ton (Mg) of gasified coal. Using that average, the gasification of 28,000 tons (25,400 Mg) of coal per day requires about 5,900 gpm (1340 m^3/hr) of water intake, which is equivalent to about 9,500 acre-ft (11.7 km^3) of water per year.

TABLE 2. GASIFICATION SULFUR BALANCES AND DISCHARGES IN FIVE OF THE PROPOSED PROJECTS
(Excluding sulfur derived from any coal fired in steam generators)

	HAMPSHIRE PROJECT	WYCOALGAS PROJECT	NOKOTA PROJECT	TENNECO PROJECT	GREAT PLAINS PROJECT
COAL GASIFIED, 10^9 Btu/D (TJ/D)	242 (255)	386 (407)	396 (418)	462 (487)	412 (435) [a]
SULFUR INPUT, T/D (Mg/D):					
In gasified coal	49.5 (44.9)	73.0 (66.2)	244.0 (221)	271.3 (246.1)	290.5 (263.5)
SULFUR OUTPUTS, T/D (Mg/D):					
As byproduct sulfur	44.0 (39.9)	66.1 (60.0)	223.7 (202.9)	249.1 (225.9)	231.4 (209.9)
In $CaSO_4$ [b]	na	nil	10.2 (9.2)	5.0 (4.5)	na
In Na_2SO_4 [c]	na	na	na	na	4.1 (3.7)
In gasifier ash	3.5 (3.2)	4.6 (4.2)	0.3 (0.27)	9.2 (8.3)	38.8 (35.2)
In product SNG	na	nil	nil	nil	nil
In product methanol	na	na	nil	na	na
In liquid products and byproducts	nil	na	3.0 (2.7)	na	0.9 (0.82)
	47.5 (43.1)	70.7 (64.2)	237.2 (215.1)	263.3 (238.7)	275.2 (249.6)
Sulfur discharges	2.0 (1.8)	2.3 (2.0)	6.8 (6.2)	8.0 (7.3)	15.3 (13.9)
	49.5 (44.9)	73.0 (66.2)	244.0 (221.3)	271.3 (246.0)	290.5 (263.5)
SULFUR DISCHARGES AS:					
Percent of sulfur input	4.0	3.2	2.8	2.9	5.3
lb of $SO_2/(10^6$ Btu of gasified coal) (ng/J)	0.03 (12.9)	0.02 (8.6)	0.07 (30.1)	0.07 (30.1)	0.15 (64.5)

[a] Total for ultimate full-size plant.

[b] Gasification sulfur outputs allocated to $CaSO_4$ occur only for those plants burning tars, oils, naphtha, phenols, lock gas, etc. in boiler plants equipped with flue gas desulfurizing scrubbers.

[c] Recovered from Stretford unit waste liquid.

na Not applicable

nil Essentially zero

TABLE 3. RAW WATER USAGE AND GAS LIQUOR TREATMENT IN FIVE OF THE PROPOSED PROJECTS

	HAMPSHIRE PROJECT	WYCOALGAS PROJECT	NOKOTA PROJECT	TENNECO PROJECT	GREAT PLAINS PROJECT
RAW WATER INTAKE:					
Gal./min(m^3/hr)	2,500 (570)	3,860 (880)	6,000 (1,360)	6,800 (1,540)	8,600 (1,950)
Tons/ton (Mg/Mg) of gasified coal	1.00 (1.00)	1.01 (1.01)	1.27 (1.27)	1.24 (1.24)	1.80 (1.80)
GAS LIQUOR TREATMENT AND FLOW SEQUENCE:					
Phenols extraction [a]	●	●	●	●	●
H_2S and NH_3 removal [b]	●	●	●	●	●
Biological oxidation	●	●	●	●	
Evaporation [c]		●			
To cooling tower as makeup water	●	●	●	●	●
Cooling tower blowdown:					
Evaporation [d]	f	●	●	f	●
Incineration	f			f	●
Disposal of residual:					
To gasifier ash quenching	●	e		●	e
To ash handling		e	●		e
To evaporation pond	●	e			e

[a] Via Phenosolvan process

[b] Via stripping process (such as Phosam process)

[c] Evaporation ahead of cooling tower, with condensate used as cooling tower makeup. Blowdown from cooling tower returns to the evaporation unit.

[d] Evaporation of cooling tower blowdown, with condensate reused inplant.

[e] The residual disposal is not made clear in the available references.

[f] Cooling tower blowdown sent directly to residual disposal.

The contaminated gas liquor generated by Lurgi coal gasification constitutes the major wastewater stream in a coal gasification plant. The quantity of dephenolized, stripped gas liquor for three of the five designs is:

Project	gpm (m^3/hr)	tons of gas liquor per ton of gasified coal (Mg/Mg)
Great Plains	4,700 (1,070)	1.0 (1.0)
Hampshire	1,700 (390)	0.7 (0.7)
WyCoalGas	3,130 (710)	0.8 (0.8)

The gas liquor treatment sequence for the five designs is also presented in Table 3. It is of interest to note that:

- All five designs use the Phenosolvan process for extracting the bulk of the phenols from the gas liquor.
- All five of the designs use a stripping process to remove hydrogen sulfide and to recover byproduct ammonia from the gas liquor. Three of the designs plan to use the Phosam stripping process and one of the designs plans to use the Chemi-Linz/Lurgi (CLL) stripping process.
- Four of the designs further treat the stripped liquor via biological oxidation prior to using the treated wastewater as cooling tower makeup. One of the designs uses the stripped liquor as cooling tower makeup without prior biological treatment.
- Three of the designs evaporate the cooling tower blowdown to recover water for inplant reuse. One of those three designs evaporates the stripped liquor and the cooling tower blowdown to obtain the cooling tower makeup.
- One of the designs incinerates the concentrate from evaporation of the cooling tower blowdown.

It is also of interest to note that a Lurgi author[12] recommends that the treatment sequence be: phenol extraction, stripping, biological oxidation, activated carbon adsorption, and ion exchange. The recommended treatment is stated to be needed prior to using the treated water as cooling tower makeup.

GAS VENTING FROM COAL LOCKHOPPERS

As discussed earlier herein, technologies such as incineration or recovery/reuse are available for gases vented from the Lurgi gasifier coal lockhoppers. Table 4 summarizes how that venting is handled in three of the designs. The venting of gasifiers during shutdown and start-up is also summarized in Table 4.

TABLE 4. HANDLING OF COAL LOCK VENTING AND OF GASIFIER START-UP/SHUTDOWN VENTING IN THREE OF THE PROPOSED PROJECTS

	GREAT PLAINS PROJECT	WYCOALGAS PROJECT	NOKOTA PROJECT
COAL LOCK VENTING:			
High pressure gas	Vented through venturi scrubber to Stretford unit for desulfurizing and then routed to the boilers for incineration.	Vented to a gas holder and recompressed back into the process gas.	The available reference documents are unclear on this point.
Low pressure gas	Vented through venturi scrubber and recompressed to join the high pressure vent gas routed to the Stretford unit and then to the boilers.	Displaced by slipstream of cooled process gas and vented to gas holder for recompression back into the process gas.	Displaced by slipstream of carbon dioxide offgas from the Rectisol unit and vented to the boiler fireboxes for incineration.
Exhaust gas	Evacuated by ejector, using motive air, and vented to atmosphere.	Evacuated by fans and incinerated in the boiler fireboxes.	Evacuated by ejector, using motive air, and vented to the atmosphere.
GASIFIER START-UP AND SHUTDOWN VENTING:			
Crude process gas	Vented to start-up incinerator.	Vented to plant flare for incineration.	It has been assumed that the plant's vent gas incinerator would also handle this service

REFERENCES:

(1) "Coal To Gasoline Plant," brochure describing Hampshire Energy Company's proposed project at Gillette, Wyoming, provided by Hampshire Energy Company by transmittal dated August 1981.

(2) Meeting and discussion with Hampshire Energy Company personnel in August 1981.

(3) Flow diagrams and fact sheet for Tenneco's proposed project in Montana, provided by Tenneco by transmittal dated August 1981.

(4) "Prevention Of Significant Air Quality Deterioration Permit Application," February 1980, submitted by Nokota Company to the North Dakota Department of Health. Provided by Dames and Moore by transmittal dated August 1981.

(5) "Air Quality Permit Application For A Proposed Coal Gasification Plant," June 1981, submitted by WyCoalGas, Inc. to the Wyoming Department of Environmental Quality.

(6) Flow diagram and process description for WyCoalGas's proposed project in Wyoming, provided by the Panhandle Eastern Pipe Line Company by transmittal dated August 1981.

(7) "Plant Sulfur Disposition, " WyCoalGas flow diagram provided to the EPA's NAPCTAC committee in 1977.

(8) "Request For Amendments To The Permit To Construct For The ANG Coal Gasification Plant (Great Plains Gasification Associates), Mercer County, North Dakota," submitted by ANG Coal Gasification Company to the North Dakota State Department Of Health, February 1979.

(9) "Final Environmental Impact Statement, Great Plains Gasification Project, Mercer County, North Dakota," U.S. Department of Energy, August 1980.

(10) Beychok, M.R., "Coal Gasification And The Phenosolvan Process," Division of Fuel Chemistry, 168th National ACS Meeting, Atlantic City, September 1974.

(11) Beychok, M.R., "Sulfur Emission Controls For A Coal Gasification Plant," EPA-600/2-76-149 (NTIS PB257-182), Symposium Proceedings: Environmental Aspects Of Fuel Conversion Technology, II, (December 1975, Hollywood, Florida), June 1976.

(12) Rolke, D., "Treatment Of Gas Liquor From Coal Gasification Plants," Lurgi Information No. 7, Vol. 6, July 1981.

Session VI: PRODUCT-RELATED CONSIDERATIONS

Chairman: Robert P. Hangebrauck
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Research Triangle Park, NC

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U.S. Environmental Protection Agency
Washington, DC

RISK ASSESSMENT OF SYNFUEL TECHNOLOGY[†]

A. Alan Moghissi
U.S. EPA
Washington, DC 20460

(No paper or abstract available.)

PREMANUFACTURE REVIEW OF SYNFUELS UNDER TSCA†

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U.S. Environmental Protection Agency
Washington, D.C. 20460

ABSTRACT

The Toxic Substances Control Act (TSCA) requires manufacturers to notify EPA at least 90 days before they produce a new chemical substance for commercial purposes. Once notified, EPA has 90 days, extendable for good cause to 180 days, to review the chemical. During the review period, the Agency can act to prohibit or limit the manufacture, processing, or use of a new chemical substance where it finds that the information available on the substance is insufficient for a reasoned evaluation of its risks and that (1) the chemical may present an unreasonable risk to human health or the environment or (2) significant human or environmental exposure can reasonably be expected. Certain synthetic fuel products (including certain byproducts and intermediates) may be new chemical substances under TSCA and therefore potentially subject to premanufacture notice requirements. This paper outlines TSCA premanufacture notification requirements; it describes how "new" chemical substances are defined; and it discusses the types of data that might be provided to EPA with a premanufacture notice on a synfuel.

INTRODUCTION

The Toxic Substances Control Act (TSCA) of 1976 was the first Federal statute addressing commercial chemicals through all phases of their life cycle -- manufacture, processing, distribution in commerce, use, and disposal -- rather than specific uses of chemicals or particular media in which they might be found. A key feature of the act, which Congress passed in response to highly publicized incidents involving chemicals like PCB's, vinyl chloride, and BCME, was its focus on prevention. By giving EPA authority to require testing on suspected chemicals and by requiring it to review new chemicals before manufacture, Congress hoped to make it possible for the Agency to act against unreasonable risks before actual harm to human health and the environment occurred, rather than to address hazardous situations only after the damage had been done.

TSCA's premanufacture notice (PMN) requirements for new chemicals epitomize this preventive approach. Under §5, companies must notify EPA 90 days before they produce a new chemical, giving EPA the opportunity to review the chemical before exposure occurs. Synthetic fuels developers, because they will be manufacturing new fuels and related products, may in some cases be subject to these requirements. We recognize that this possibility has raised considerable concern in the synfuels industry.

Because of this concern, the EPA Office of Toxic Substances, which is responsible for administering TSCA, is committed to working with industry to clarify TSCA requirements and to ensure that premanufacture notice requirements do not unnecessarily delay the development of synfuels. Toward this end, we have met with several trade organizations and private companies to address both general and specific concerns, and we are cooperating with other offices in EPA and other government agencies to avoid duplication and to ensure a consistent approach. In carrying out our responsibilities under TSCA, we will be careful to avoid constructing artificial barriers to development -- that is, those that do not contribute to results with substantial health or environmental benefits.

In the remainder of this paper, we discuss in more detail TSCA's premanufacture notice requirements, the applicability of these requirements to synthetic fuels (in particular, coal-based fuels), and the types of data that manufacturers might develop in preparing a PMN.

SECTION 5 PREMANUFACTURE NOTICE REQUIREMENTS

Section 5(a) of TSCA requires companies to notify EPA at least 90 days before beginning to manufacture or import a "new chemical substance" for commercial purposes. As explained later, new chemical substances are defined under the Act as substances not listed on EPA's Chemical Substance Inventory, a compilation of chemicals in commercial production first published in 1979. Once notified, EPA has 90 days, extendable for good cause to 180 days, to review the potential risks likely to be posed by the new substance.

During the review period, EPA can act under §5(e) to prohibit or limit the manufacturing, processing, distribution, use, or disposal of the substance, pending the development of data, if it finds that the information available on the substance is insufficient for a reasoned evaluation of its health and environmental effects *and* that (1) the chemical *may present* an unreasonable risk to human health or the environment or (2) significant human or environmental exposure can reasonably be expected. If the Agency finds that the substance *will present* an unreasonable risk, it can regulate it under §5(f). When EPA does not take action under §5(e) or §5(f) during the review period, manufacture or import can begin without restrictions. After commercial manufacture begins, the substance is added to the inventory. At that point, the substance is no longer "new," and other manufacturers are free to produce it without submitting a PMN.

Section 5(d) of TSCA specifies the information that must be included in a PMN. In general, manufacturers must provide known or "reasonably ascertainable" information on chemical identity, anticipated production volume, categories of use, byproducts, workplace exposure, and manner or methods of disposal.* They are also required to provide test data that they have already developed and to describe any other information on health and safety they know or can "reasonably ascertain." However, TSCA -- unlike laws regulating the introduction of pesticides or drugs into commerce -- imposes no mandatory testing requirements for new chemicals.

The key to EPA's review of new chemicals under TSCA is the concept of "unreasonable risk." The Agency has not developed any general criteria for determining "unreasonable risk," because the finding depends too much on the specific situation. The Agency's approach to determining unreasonable risk, however, is illustrated in Figure 1. Potential toxicity (including ecotoxicity) and exposure define the risks a substance presents under specific circumstances of manufacture, processing, distribution, use, or disposal. To determine whether these risks are "reasonable," the Agency balances them against the benefits to be derived from the product, the cost of measures necessary to reduce risks, the availability of substitutes, and the comparative risks posed by products they may replace in the market.

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* Some of the information submitted in a premanufacture notice may be confidential, including highly sensitive business information. The Office of Toxic Substances routinely handles such information under TSCA, and it has established elaborate procedures (including serious penalties) to prevent its disclosure.

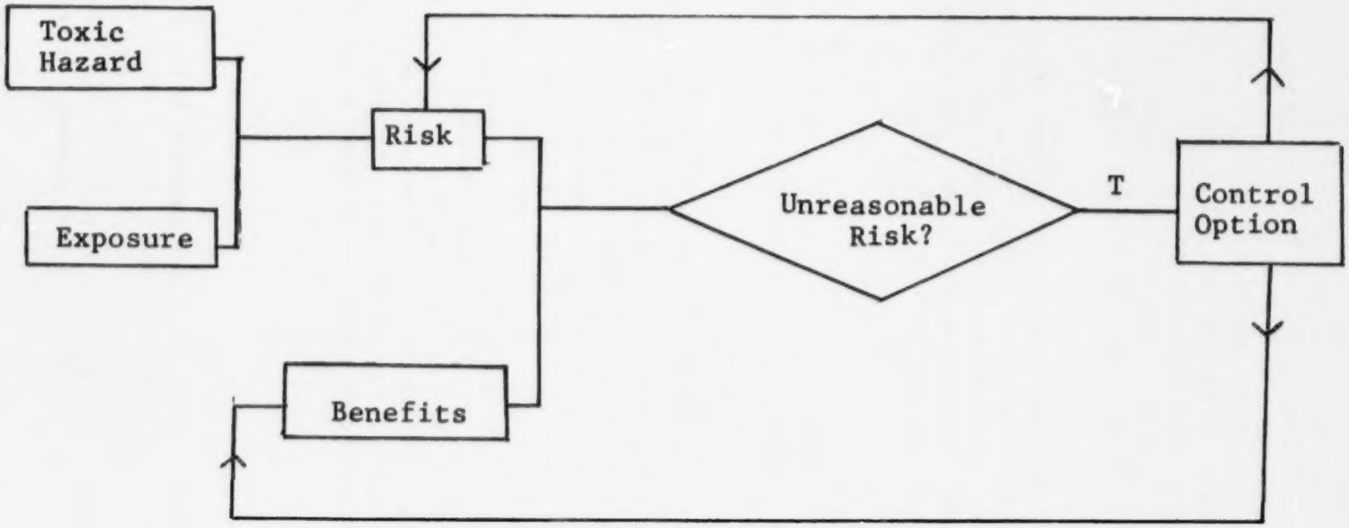
Toxic Hazard
Exposure
Risk
Benefits
Unreasonable Risk?
T
Control Option

Figure 1. Determination of Unreasonable Risk Under TSCA

Several points about the review of new chemicals under TSCA §5 that are often misunderstood, particularly by companies more familiar with EPA permitting offices, should by now be clear. First, §5 imposes a notification requirement; it does not set up a licensing or registration program. To limit or halt production, EPA must take positive action against a chemical, based on certain specific findings. Otherwise, the chemical can enter commerce unregulated. Consequently, the Agency has in no sense "approved" a chemical that it has not regulated under §5. Second, TSCA does not impose testing requirements on manufacturers of new chemicals. Instead, the manufacturer of a new chemical has the responsibility to determine what level of testing, if any, is appropriate for a chemical, given its composition and projected uses. Finally, the "unreasonable risk" standard of TSCA incorporates the principle that the risks of a chemical can only be evaluated meaningfully within the context of the benefits derived from it and the costs of regulation. EPA's goal under TSCA is to balance these considerations rather than to reduce risk to some absolute "acceptable" level or to impose some other standard, such as best available technology.

To date, EPA has reviewed more than 800 new chemicals under the premanufacture review program. All these have been general industrial chemicals, such as intermediates, dyes, photographic chemicals, and lubricant additives. None has been a synthetic fuel. Therefore, it is difficult to make observations on synfuels and PMN requirements based on the history of the PMN program to date. Several special features of synfuels will distinguish them from new chemicals previously reviewed in the PMN program and raise particular issues for the PMN review process and for companies submitting notices. These features include:

- The national interest in alternate fuels development and energy independence

- The tremendous investments in synfuels development before commercialization

- The staged development of synfuel projects, which may include process and product changes in the course of commercialization, and therefore may complicate the task of characterizing the product and its toxicity

- The large production volume projected for synfuels, the potential for exposure to some commercial fuel products, and the presence of potentially toxic substances in some synfuel products

- The difficulties involved in evaluating health and environmental effects of complex, multicomponent substances like synfuels

- Public concern about potential hazards from synfuels

Because of the importance of synfuels projects and the money committed to them, developers subject to PMN requirements are encouraged to consult EPA well before PMN submission to ensure that they are developing information sufficient for a reasoned evaluation of risk. In this way, EPA and industry can ensure that the PMN process will not unecessarily delay the commercialization of a product.

PMN REQUIREMENTS AND SYNFUELS

Some synfuels developers -- and companies refining new synfuels -- may be intending to make products that would be "new chemical substances" subject to TSCA premanufacture notice requirements. OTS is now reviewing the applicability of §5 requirements to synfuels (for example, how the research and development exemption of §5(h)(3) should apply to projects of this scale), and it is developing a consistent approach to defining and characterizing synfuel products, so that industry can readily determine whether a specific product is new. Although this work is not yet completed, it is possible at this point to provide developers some preliminary guidance on the Office of Toxic Substances' current thinking on premanufacture notice requirements for synfuels. For more specific guidance, we recommend that individual developers consult the Office.

WHEN IS A PMN REQUIRED?

The PMN Requirement Is Substance-Specific

"Chemical substances" have a special definition under TSCA -- the term covers both discrete chemical compounds (e.g., benzene or sodium chloride) and complex substances produced by chemical reaction (e.g., coal tar or slag), including refined products (e.g., petroleum distillates). However, the term excludes "mixtures" that could be produced for commercial purposes by combining substances without a chemical reaction. Complex materials such as typical coal liquids are not considered "mixtures" under TSCA, but rather are chemical substances, because they could not practicably be made by mixing their constituents.

TSCA premanufacture notice requirements apply to such "substances" if they are new. In this respect, these requirements differ from permitting requirements, which apply to facilities rather than chemicals. A new facility producing "existing" substances would not be subject to PMN requirements. On the other hand, a single facility is likely to produce several products, any or all of which might be "new" and therefore subject to PMN.

"New" Chemical Substances Are Chemicals Not Listed on the TSCA Chemical Substance Inventory

Under §8(b) of TSCA, EPA has compiled and keeps current an inventory of chemical substances in commerce, first published in June 1979. Chemicals listed on the inventory are considered "existing" substances, not subject to PMN notice requirements. When chemicals complete PMN review and enter commercial production, they are added to the inventory. Therefore, manufacturers may determine whether their substances are new by consulting the list or, where questions of product identification are difficult, by asking the Office of Toxic Substances whether the substances are listed.

The Substance Must Be Manufactured or Imported "For Commercial Purposes"

TSCA §5 requirements specifically apply to chemical substances manufactured "for commercial purposes." This includes intermediates and other chemicals consumed entirely on the site at which they are manufactured. As a result, intermediate streams used in making new synthetic fuels may be subject to PMN requirements, even if they are never sold or distributed in commerce.

Research and Development Chemicals Are Exempt From PMN Requirements

Chemicals manufactured "only in small quantities" solely for research and development are specifically exempted from PMN requirements by §5(h)(3) of the Act. Activities falling within the category of R&D include the evaluation of the physical, chemical, production, and performance characteristics of a substance. Thus, pilot plant operations designed to assess manufacturing or refining processes, test burns to evaluate fuel efficiency or emissions, and other product characterizations are possible without a PMN. These evaluations may be carried out by people other than the manufacturer, including potential industrial customers. Furthermore, the sale of a product to a potential customer who will use it only for R&D does not remove the product from the category of R&D. EPA has not placed a specific volume limit on the R&D exemption, but rather has stated that "only in small quantities" means only in quantities no greater than reasonably necessary for R&D (see 40 CFR 710.2(y)). For synfuels, because of the nature of R&D activities, "small quantities" may be large compared to production volumes for typical industrial chemicals.

Nonisolated Intermediates Are Exempt

Chemical intermediates not intentionally removed from the equipment in which they are manufactured are exempt from PMN requirements. (See 40 CFR 710.4(d)(8).) As a result, non-isolated process streams in a synfuels plant are not subject to these requirements. However, if the intermediate stream is removed from the plant equipment -- including for storage -- it may be subject.

Some Commercial Byproducts Are Exempt

The inventory reporting rules exempt from PMN requirements byproducts that have commercial value only to organizations who (1) burn them as fuel, (2) dispose of them as waste, including in a landfill or for enriching soil, and (3) extract component chemical substances from them. (See CFR 710.4(d)(2).) Under this provision, certain byproduct streams burned for process heat as an alternative to disposal may be exempt from PMN require ments -- for example, phenols produced as a byproduct of coal gasification would not be subject to PMN if incinerated.

HOW CHEMICAL SUBSTANCES ARE DEFINED

When EPA compiled the initial TSCA inventory, it faced a number of complex issues related to chemical identification and nomenclature. The resolution of these issues, reflected in the way products were reported for the inventory and how they are listed, now defines the Agency's approach to defining products for PMN purposes.

For single-component substances that can be characterized by a molecular formula -- like ammonia, benzene, and methanol -- the problem of identification was simple. These products are listed on the inventory under their chemical names; manufacturers of the substances, therefore, are not subject to PMN requirements, regardless of how the substances are made and what levels of impurities they contain.

Complex reaction products -- for example, materials produced in coking coal or refining petroleum -- presented a very different problem. Here, the products could not be defined by a single structure or an unambiguous chemical name. Instead, these products were defined by source material and process of manufacture rather than by compositional data alone. An attempt was made to define product categories broadly enough so that limited variations in source (e.g., substitution of one grade of coal or one petroleum crude for another) or slight changes in process did not create a new product, but at the same time narrowly enough so that substances within a product category could be expected to be similar in composition and biological activity.

This approach can best be illustrated by the listing of refined petroleum products on the inventory. For example, the inventory entry "light hydrocracked distillate (petroleum)" is defined as "a complex combination of hydrocarbons from the distillation of the products of a hydrocracking process. It consists primarily of saturated hydrocarbons having carbon numbers predominantly in the range of C_{10} through C_{18}, and boiling in the range of 160°C to 320°C." This description, it can be seen, identifies the source material (petroleum), the process of manufacture (hydrocracking and distillation), and composition (C_{10}-C_{18} saturated hydrocarbons) as well as a physical property (boiling range) that roughly correlates with chemical composition. Any hydrocarbon product that met these criteria would be considered the same product for inventory purposes and therefore would not be subject to PMN. Comparable products from a different source material or manufactured by a different process, however, would be different chemical substances under the inventory rules. (Other examples of petroleum products are given in Table 1.)

This discussion should make it clear that, for TSCA inventory purposes, coal-derived synthetic fuels are, a priori, different chemical substances from petroleum-based fuels. An inventory entry for petroleum naphtha, for example, would not cover a naphtha derived from coal, even if the general composition and the boiling range of the products were similar, because their source materials are different. In the same way, a naphtha derived from coal gasification is not comparable to a naphtha derived from the solvent-refining of coal, because of the clear difference in process. Therefore, a PMN might be required for a naphtha produced in a high-Btu coal gasification operation even though petroleum naphtha and coal naphtha produced by pyrolysis were listed on the inventory. (However, we recognize that at some point in refining coal, oil shale, and petroleum products becomes so similar that source should no longer be a factor in product definition.)

The Office of Toxic Substances is now working to develop product definitions for synfuels comparable to definitions

TABLE 1. SAMPLE PETROLEUM PRODUCT DEFINITIONS ON THE TSCA CHEMICAL SUBSTANCE INVENTORY (FROM TOXIC SUBSTANCES CONTROL ACT)

CRUDE OIL DISTILLATION STREAMS

Light Straight Run Naphtha (Petroleum) [*64741-46-4]

A complex combination of hydrocarbons produced by distillation of crude oil. It consists predominantly of aliphatic hydrocarbons having carbon numbers predominantly in the range of C_4 through C_{10} and boiling in the range of approximately minus 20°C to 180°C (-4°F to 356°F).

Heavy Straight Run Naphtha (Petroleum) [*64741-41-9]

A complex combination of hydrocarbons produced by distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly in the range of C_6 through C_{12} and boiling in the range of approximately 65°C to 230°C (149°F to 446°F).

Straight Run Kerosine (Petroleum) [*8008-20-8]

A complex combination of hydrocarbons produced by the distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly in the range of C_9 through C_{16} and boiling in the range of approximately 150°C to 290°C (320°F to 554°F).

Straight Run Middle Distillate (Petroleum) [*64741-44-2]

A complex combination of hydrocarbons produced by the distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly in the range of C_{11} through C_{20} and boiling in the range of 205°C to 345°C (401°F to 653°F).

Straight Run Gas Oil (Petroleum) [*64741-43-1]

A complex combination of hydrocarbons produced by the distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly in the range of C_{11} through C_{25} and boiling in the range of approximately 205°C to 400°C (401°F to 752°F).

OTHER PRODUCTS

Light Hydrocracked Distillate (Petroleum) [*64741-77-1]

A complex combination of hydrocarbons from the distillation of the products from a hydrocracking process. It consists predominantly of saturated hydrocarbons having carbon numbers predominantly in the range of C_{10} through C_{18}, and boiling in the range of approximately 160°C to 320°C (320°F to 608°F).

Hydrotreated Light Distillate (Petroleum) [*64742-47-8]

A complex combination of hydrocarbons obtained by treating a petroleum fraction with hydrogen in the presence of a catalyst. It consists of hydrocarbons having carbon numbers predominantly in the range of C_9 through C_{16} and boiling in the range of approximately 150°C to 290°C (302°F to 554°F).

Light Catalytic Cracked Distillate (Petroleum) [*64741-59-9]

A complex combination of hydrocarbons produced by the distillation of products from a catalytic cracking process. It consists of hydrocarbons having carbon numbers predominantly in the range of C_9 through C_{25} and boiling in the range of approximately 150°C to 400°C (302°F to 752°F). It contains a relatively large proportion of bicyclic aromatic hydrocarbons.

Crude Phenolic Compounds (Petroleum) [*64743-03-9]

A complex combination of organic compounds, predominantly phenol, cresols, xylenols and other alkylated phenols obtained primarily from cracked naphtha or distillate streams by alkaline extraction.

Vacuum Residuum (Petroleum) [*64741-56-6]

A complex residuum from the vacuum distillation of the residuum from atmospheric distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly greater than C_{34} and boiling above approximately 495°C (923°F).

already developed for petroleum products. The goal is to divide the spectrum of potential synfuel products into generic chemical substance categories that will be unambiguous both to industry and EPA and that will reflect likely compositional differences. This scheme would define how new synfuels would be listed on the inventory. As a result, it would make it possible to determine which products should be considered equivalent to existing products for PMN purposes and might be subject to PMN requirements. Specifically, OTS is addressing questions like: Are products from different coal liquefaction processes (e.g., SRC-II, EDS, and H-coal) likely to be sufficiently similar in composition and biological activity to justify their treatment as the same substance for inventory and PMN purposes? (In other words, if an SRC-II liquid is entered on the inventory, would a comparable EDS or H-coal product automatically become an existing substance not subject to PMN?) At what point in the refining process should synfuel products be considered essentially equivalent to comparable petroleum products and therefore not be subject to PMN requirements? In this work, OTS has solicited information and advice from the American Petroleum Institute, and it is in contact with the National Council on Synthetic Fuels Production. The Office is also willing to meet with other organizations or individual companies who have an interest in these questions.

Until this work is completed, it is difficult to provide definitive answers to questions about whether one synfuel product should be considered equivalent to another for PMN purposes, or how many synfuels are likely to be subject to PMN requirements. It is possible, nevertheless, to provide some guidance on requirements for certain specific products. For example:

1. Sulfur, ammonia, and carbon dioxide produced in the gasification or liquefaction of coal are existing substances and thus are not subject to PMN requirements.

2. Methanol produced from coal is equivalent to methanol listed on the inventory and thus is not subject to PMN. However, indirect coal liquids are not on the inventory and therefore may be subject to PMN requirements if manufactured for commercial purposes.

3. Substitute natural gas produced by coal gasification is predominately methane, which is listed on the inventory, and therefore is not subject to PMN.

4. SRC I wash solvent, SRC I mineral residue, and SRC naphtha, which are listed on the inventory, are not subject to PMN requirements. Other SRC products reported

for the inventory are under review by OTS, as described below.

Because of the complexity of product definitions, we encourage synfuel developers to consult OTS on the applicability of PMN requirements to their products.

STATUS OF SYNFUELS REPORTED FOR THE INVENTORY

Under the previous administration, OTS began a review of 20 synfuel products (9 SRC products and 11 oil shale products) reported for the inventory to determine if they should have been included on the list. The key question was whether the products had been manufactured for purposes other than research and development during the period when the inventory was compiled. OTS has determined that certain of the products -- including the SRC products listed under item number 4 above -- had in fact been properly listed. For the other products, OTS decided that it did not have enough information to make a determination, and it asked for further information from the companies that had reported them for the inventory. We anticipate that the Agency will decide the status of these products in the near future.

PMN SUBMISSIONS

As previously discussed, TSCA requires PMN submitters to provide certain information on chemical identity and exposure, but it does not require manufacturers of new chemical substances to develop health and safety data specifically for their notices.* However, §5(e) gives EPA the authority to delay the commercial production of a new chemical in the absence of data necessary for a reasoned evaluation of the chemical's health and environmental effects -- if the substance "may present an unreasonable risk" or that there will be "significant or substantial exposure" to it.

The nature of this §5(e) authority, and EPA's interpretation of it, has raised concern among some prospective synthetic fuel producers. Several companies have asked OTS to identify the data it would consider sufficient for a "reasoned evaluation" of a particular synfuel and to comment on the appropriateness of specific test plans. To address such questions, the Agency has established a Synfuels/Toxics Workgroup, managed by OTS, which can provide guidance to individual producers and will facilitate the review of PMN's on synfuels. Synfuels developers are encouraged to discuss questions concerning data development and methods of controlling risks with this group before submitting a PMN.

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* For general guidance on EPA's interpretation of premanufacture notice requirements, see Toxic Substances Control: Premanufacturing Notification Requirements and Review Procedures; Statement of Interim Policy (44 FR 28564, May 15, 1979) and Toxic Substances Premanufacture Notification Requirements and Review Procedures: Statement of Revised Interim Policy (45 FR 74378, November 7, 1980).

Because there are no testing requirements under TSCA for new chemicals, EPA has not developed prescriptive guidelines for data development on synfuels. In addition, it is difficult to define a single approach for different products because, among other reasons, the specific composition of a product and the conditions of its production and use will influence how much and what types of information might be appropriate. However, we believe that the following general principles are applicable to any program evaluating risks from synthetic fuels:

- Data should be appropriate to what is known about chemical composition and exposure. For example, if exposure is limited, limited data may be sufficient for a reasoned evaluation.

- Full characterization of risks before a synfuel is manufactured commercially may in some cases be infeasible. Although the amount of data available may be limited early in commercial development, concern for risk posed by a substance would be limited by the fact that exposure and production volume are relatively low. However, as a substance grows in the market, more data might in some cases be appropriate.

- New synthetic fuels should be evaluated in comparison to the petroleum products they would replace to provide a perspective on the risks they might present. If replacing petroleum products by a synfuel will not lead to an increase in risk, risks from the new synfuel should generally be considered reasonable.

In the remainder of this presentation, we will describe in somewhat more detail the kinds of thinking that typically goes into a risk evaluation and that lies behind OTS' general approach to assessing data provided in a PMN.

CHEMICAL CHARACTERIZATION

In many cases, the chemical composition of a product -- including the extent to which it contains minor constituents of known or suspected toxicity, like aromatic amines, heterocyclic nitrogen compounds, and PNA's -- can serve as an important guide in determining what data are appropriate for evaluating risks. For example, a chemical analysis of a gasoline derived from indirect liquefaction might show that it was less aromatic and more aliphatic than typical petroleum gasolines, and contained a considerably lower level of toxicologically significant constituents. This could provide a rationale for limiting the extent of toxicity testing. At the same time, extensive testing of substances known to be highly hazardous may be redundant. For example, if a coal-derived residual fuel contained significant quantities of known or suspected carcinogens, the premanufacture review of this substance would focus on potential exposure and the manner of uses to establish that risks are adequately controlled.

EXPOSURE ASSESSMENT

Conditions of exposure are also an important factor in deciding what health and environmental-effects data would be appropriate to evaluate risks posed by a specific substance. Typically, exposure assessments address direct exposure to humans, indirect exposure to humans from environmental release, and exposure to the environment during all phases of a substance's life cycle -- manufacture, handling, distribution, storage, and end use. Anticipated production volume for different uses, potential targets of exposure, and magnitude of exposure are also factors that often guide data development. We recognize that there is no simple formula for translating such considerations into a testing strategy. However, in reviewing PMN's on new chemicals, the Agency evaluates the data presented in the light of exposure-related considerations.

It is possible to illustrate in general terms how different exposure scenarios might influence data development. The following uses, for example, would on the whole reflect increasing levels of direct human exposure: industrial boiler fuel, diesel transport fuel, and consumer gasoline. EPA's review of health and environmental effects data on products within each of these categories would consider the different levels and modes of exposure -- where exposure is likely to be higher, data should provide greater certainty that a substance does not present an unreasonable risk. As a second example, tentative or preliminary data might be reasonable for products made in early-term plants, if the products would be used in a restricted or controlled manner.

EXISTING DATA

The Department of Energy, EPA, private companies, and other organizations have developed a considerable amount of information relevant to risks that may be posed by new synfuels. This includes data on the toxicity of comparable petroleum and synfuel products, exposure information on different fuel uses, information on the use of specific toxicity tests for complex mixtures like synfuels, toxicity data on chemicals likely to be found in a synfuel, and similar information. PMN submitters should consider the implications of this information in determining what and how much data they should develop.

TOXICITY AND ENVIRONMENTAL EFFECTS TESTING

As we stated before, TSCA does not require the testing of new chemicals. In addition, because the review of risks posed by a new synfuel will depend on the specific product and its projected uses, it is impossible to develop prescriptive guidelines for health and environmental effects data. Instead, synfuels developers are encouraged to discuss their products and testing plans with the Office of Toxic Substances before PMN submission.

OTS recognizes that the scale and scheduling of many synfuel projects are likely to make it difficult for developers to provide final health and environmental-effects data sufficient for evaluating risks associated with a full-scale commercial operation at the time they submit a premanufacture notice. For example, if a manufacturer is conducting long-term tests, results might not be available at the time of notice submission. In addition, products are likely to change in scaleup or as a result of process changes; in some cases, pilot-plant material available for toxicity testing may not be comparable to products later made in a commercial plant. Thus, if tests are being conducted on early-stage products, the relevance of the results of these tests to an evaluation of the potential effects of final commercial products should be considered. In such circumstances, technical judgment can be used to evaluate whether the final product is likely to present more or less of a problem than the tested material.

EPA understands that it is often common for the development of data to proceed as technology develops and commercial samples become available. It is possible, of course, that a commercial substance might later prove to be more hazardous than initially believed, or that subsequent data might show that the substance would present an unreasonable risk under certain circumstances. Companies developing a new product would typically have contingency plans for controlling exposure in this situation. These plans, for example, might call for restricting uses; imposing engineering controls; upgrading the product; changing the process or product slate; or similar measures. In reviewing PMN's on new synfuels, EPA will consider all these factors in assessing the reasonability of risk.

By early consultation with EPA about PMN-related issues, synfuels developers can ensure that PMN requirements do not unnecessarily delay the commercialization of their products, and that any differences on appropriate data development are resolved before formal PMN submission.

CONCLUSION

The evaluation of risks posed by synthetic fuels raises a number of complex issues. We cannot expect to achieve perfect certainty in this area, nor can we hope to eliminate all risk. Instead, EPA's standard under TSCA is "unreasonable" risk, which takes into account potential benefits, availability of substitutes, and risks posed by comparable products in society. Under §5, EPA has the responsibility to review new chemicals according to this standard before they enter commercial production. However, we recognize the unique issues raised by the premanufacture review of synfuels. Where PMN requirements apply to new synfuels, the Agency will work with developers to ensure that these requirements do not unduly impede technological innovation, while protecting health and the environment from unreasonable risk.

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METHANOL AS A CLEAN MAJOR FUEL

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ABSTRACT

The objective of this investigation of methanol as a major fuel was to provide perspective for officials of the U.S. Environmental Protection Agency's Industrial Environmental Research Laboratory at Research Triangle Park regarding possibilities for commercialization and the environmental implications associated with wide use of methanol as a substitute for petroleum-derived fuels.

It is recognized that the future of methanol fuel will ultimately be determined by economics. To gain widespread acceptance, methanol will have to be cheaper than competitive fuels after all advantages and disadvantages have been considered. No attempt is made here, however, to assess the competitiveness of methanol fuels at present prices for crude oil or to project the price at which they could be competitive. Such evaluations would be far beyond the scope of the study. Instead, the methanol fuels are considered relative to other fuels that might be used if an effort is launched to apply available technology to displacement of petroleum fuels as soon as possible. The major factors considered are:

1) Potential environmental consequences of introducing methanol.
2) Status of development of methanol fuel technology.
3) Cost and efficiency of synfuel processes.

4) Potential markets.

5) Prospects for commercialization of methanol fuels.

The intent is to develop an overview perspective by identifying all important factors in each category and presenting enough quantitative data to permit relative comparisons, without excessive detail.

BACKGROUND

At present there is concern over the rate of progress in development of advanced coal conversion processes for a synthetic fuels industry. One of the principal impediments is the inflation associated with a cost-spiral driven by continuing increases in the cost of oil and other fuels, including coal.

Because of the inflationary trend, many believe that plants that could be built now to use available technology will be cheaper to operate than plants built later to use improved processes that might come onstream in a few years. Also there is a continuing concern over America's continuing dependence on foreign oil. These factors have combined to create interest in utilizing immediately applicable coal conversion technology.

The only proven coal conversion technology is indirect liquefaction; that is, the conversion of coal to synthesis gas and subsequent conversion of this gas to liquid fuel. The proven routes for coal conversion include (1) the Fischer-Tropsch process, which converts synthesis gas directly to gasoline and other byproducts, and (2) a number of catalytic processes, which convert synthesis gas to methanol. Although the Fischer-Tropsch process has the advantage of producing gasoline directly, it has the disadvantage of producing many coproducts and byproducts, which must be marketed. Methanol may be used directly, as a premium fuel, in some applications, but may have to undergo subsequent conversion to gasoline, at some added cost, for use as a transportation fuel.

If a decision is made to build synthetic fuel plants with presently available technology, the Fischer-Tropsch process and methanol fuel processes will likely be used. The Fischer-Tropsch products are essentially the same as petroleum-derived fuels, so that their introduction into commerce would not require significant adjustment. In contrast, the introduction of methanol as a major fuel would require significant adjustment.

METHANOL AS FUEL: ENVIRONMENTAL IMPLICATIONS

Although some testing has been carried out to evaluate the use of methanol as a major fuel for automobiles and stationary sources, work to evaluate the potential environmental effects has not been extensive. Whereas some properties of methanol make it attractive as a fuel, others present problems. Experimental work to date has been encouraging, but many questions remain unanswered. Following are some of the more important environmental considerations.

1) Methanol has a lower flame temperature than petroleum-derived products. It also has wide limits of combustibility. These properties combine to make either automobiles or stationary sources that are designed for methanol fuels relatively lower emitters of nitrogen oxides.

2) Methanol combustion is essentially particulate-free. No carbon-to-carbon bonds are present to promote soot formation, which is associated with burning of petroleum-derived fuels.

3) Because sulfur in the feedstocks for methanol is removed in processing, combustion of methanol generates virtually no sulfur emissions.

4) Because of its high octane rating, methanol can be used in motor vehicles without additives, eliminating the emissions associated with additives to petroleum-derived fuels.

5) Methanol's low heat content (about half that of gasoline on a volumetric basis) necessitates the use of twice the volume and over twice the weight of fuel when it is substituted for gasoline or distillate oil.

6) Some methanol properties such as corrosivity, toxicity, and explosivity call for careful consideration. Although they have not caused problems in the closely controlled situations where methanol has been used as a commercial chemical, they must be given careful attention if it is widely used as a major fuel.

7) Other environmental considerations that have not been evaluated are the reactivity, persistence, and sensory detectability of methanol in the environment. These factors could be of great importance for a chemical with potential for release in large amounts to the environment, as illustrated by the experiences with oil spills. The high solubility of methanol in water suggests that spills of methanol would not persist as oil spills do. On the other hand, the contamination of lakes or major rivers with a toxic material that disburses into water could cause fish kills and also could produce water contamination that would not be readily detected without special precautions.

The most extensive body of experimental work on methanol as a fuel has dealt with its use as a gasoline substitute. Most attention has been given to methanol-gasoline mixtures, but consideration has also been given to the use of 100 percent methanol fuel for automobiles. Although it has been established that methanol could be substituted for gasoline, there is considerable controversy over advantages and disadvantages of doing so. Some researchers expect that methanol will give higher efficiency, improved performance, and reduced pollution.[1] Others claim the opposite on all or some of these points.[2,3] It is generally accepted, however, that the use of methanol in engines designed to take advantage of its high octane and unusual combustion characteristics would give performance as good as, or superior to that of gasoline on an equivalent Btu basis.

Experimental work with methanol as a fuel for use by stationary sources has been encouraging. Tests in which methanol fuel was fired in a utility boiler designed to burn natural gas or distillate oil showed methanol to be a superior fuel.[4] Concentrations of pollutants in the combustion gases were very low (no particulates, no sulfur oxides, and low nitrogen oxides). Also, the methanol fuel burned efficiently with a stable flame, and carbon previously deposited by oil burning was burned off of heat transfer surfaces with a resultant improvement in heat transfer. Tests of methanol fuels in commercial combustion turbines were also promising. Performance was excellent, and nitrogen oxide emissions were lower than those produced by firing natural gas. Studies of methanol as a turbine fuel for combined-cycle plants were also promising, and it has been suggested that such plants could be designed to be virtually pollution free.[5]

Consideration of methanol as a fuel for nonutility stationary sources led to the conclusion that it could replace distillate oil in home heating and would give increased efficiency. This study also concluded that methanol fuels could replace gas or distillate oil in commercial and industrial applications if due consideration is given to potential problems associated with its toxicity and flammability.[6]

In summary, past work indicates that methanol has potential for wide use as a high-quality environmentally attractive fuel. The studies also show clearly, however, that its use as a fuel will require special measures for environmental protection.

STATUS OF DEVELOPMENT FOR METHANOL FUEL PRODUCTION PROCESSES

All of the technology necessary to produce methanol for fuel use is proven. At present chemical-grade methanol is produced in amounts estimated at 30,000 ton/day. Most is produced from synthesis gas made from natural gas. The largest plant in operation today is a 2500-ton/day single-train plant, which has been operational for 10 years. Plants twice this large are now considered feasible. It is claimed that because of reduced quality requirements and improvements in technology, a 5000-ton/day plant for production of fuel-grade methanol would be only slightly larger than the operating plant producing 2500 ton/day. It is further suggested that methanol fuel plants should consist of 5 trains of 5000 ton/day each in capacity.[7]

Technology for production of synthesis gas from coal is also being applied widely outside of the United States. Lurgi and Koppers-Totzek coal gasifiers are the most discussed for use in commercial production of liquid fuel from coal. Both types have a long history of application in service of the general type required for production of methanol fuels, and both have been incorporated in planned installations.

The development of the Mobil-M process, which is said to convert methanol to gasoline with an efficiency of 95 percent, may be the key to avoidance of distribution and handling problems that might otherwise impede the application of methanol fuel technology.[8] The process was announced in 1976. Since then a 4-bbl/day pilot plant has been operated. Economic comparisons with commercially established Fischer-Tropsch units are claimed to show that the Mobil process is the most promising route from coal to gasoline.[9] Construction of a plant to convert methane-derived methanol to 12,500 bbl/day of gasoline is expected to begin in late 1981 in New Zealand. The plant, to be completed in the mid-1980's, will supply an estimated 1/3 of that country's transportation fuel.

Although all major components for production of methanol fuel from coal are proven technology, no plant has yet been built. Construction of such a plant would involve making the connection between coal gasifiers producing synthesis gas and methanol plants for the first time. Also, economy of scale would require the design of methanol trains larger than any yet built. And coal would be gasified on a scale unprecedented except in South Africa, where the "Sasol I" plant employing Fischer-Tropsch technology has operated since 1955. This plant employs thirteen gasifiers, each 12 feet in diameter. Proposed plants will be even larger. Sasol II, which came on stream recently, employs 36 gasifiers.[10] The problem associated with adaptation of processes and large scale operation should not present serious technical problems, but any element of risk has potential for making investors cautious about investing in multi-billion dollar plants.

COST AND EFFICIENCY OF METHANOL FUEL PROCESSES

The attractiveness of methanol fuels over fuels from alternative processes will depend primarily on cost. The thermal efficiency of the conversion process will be an important factor in the final production cost. Comparisons of both cost and efficiency of alternative production routes are complicated by the dependence of both on the quality of feed materials and the markets for potential products and coproducts. This is illustrated in Table 1, which shows a comparison of plants employing Lurgi gasification for production of methanol, Mobil M-gasoline, and Fischer-Tropsch synthesis, with and without, coproduction of SNG.[11] The column for efficiency shows the percentage of the input Btu that comes out as product. The last column shows investment cost in dollars per million Btu output per year. The lower efficiency and higher cost shown where SNG is not a product reflect losses associated with conversion of methane formed in gasification to synthesis gas for conversion to additional liquid product.

Table 1. Efficiency of Investment Cost Indirect Coal Liquefaction[11]

	Efficiency, %	Investment Cost, $\$/10^6$ Btu/yr
Methanol from Syn Gas		
Methanol	50.8	28.2
Methanol + SNG	60.4	21.8
Methanol - Mobil M		
Gasoline	48.7	34.3
Gasoline + SNG	58.2	24.0
Fischer-Tropsch		
Gasoline + diesel	35.7	45.3
Gasoline + diesel + SNG	50.8	25.2

The cost of production of liquid fuels is frequently given in dollars per million Btu in all products. Because this approach fails to account for differences in the value of the end products, however, it can give a distorted perspective of the potential for a given technology to satisfy present needs. Also, costs are often compared without due consideration of uncertainties attributable to stage of development. One recent study, however, generated data that give some feeling for the importance of these uncertainties in comparison of technologies.[12] Data from that report are shown in Table 2. The confidence index in Column 1 has two components: a letter indicating stage of development and a number indicating the estimated reliability of the cost. The energy cost is based on the total energy value for all products. The "reference price" is based on Btu outputs, adjusted downward in proportion to their value relative to gasoline for all products that are less valuable.

Data such as these must be considered approximations subject to variation not relating to the skill or objectivity of the estimators. They do, however, highlight several important points that are creating pressure to use presently available technology as a basis for beginning the development of a synthetic fuels industry:

1) Fischer-Tropsch and methanol fuels are more costly than new processes are expected to be. The estimated costs, however, are more reliable (as indicated by the confidence index) than those for the four developmental processes.

2) The cost advantages of developmental processes are not great. Unforeseen circumstances or inflation during the developmental period could cause them to be more expensive than plants that could be built now.

3) When credits are applied for quality of product, the relative economics change significantly. The net result is that methanol shows the lowest reference price and a confidence index better than that for any other process except Fischer-Tropsch.

TABLE 2. COST COMPARISON FOR ALTERNATIVE PROCESSES FOR PRODUCTION OF LIQUID FUELS FROM COAL[12]

	Confidence index*	Energy cost, $\$/10^6$ Btu	Reference price, $\$/10^6$ Btu
Fischer-Tropsch	A-2	4.99	5.52
Methanol	A-2	4.32	4.54
Mobil M-Gasoline	C-3	4.84	4.91
Exxon donor solvent	C-3	3.96	5.40
H-coal	C-2	3.58	4.81
SRC II	B-4	3.62	5.59

* Confidence index factors:

Process development	Economic reliability
D - Exploratory stage - not beyond simple bench tests	4 - Screening estimate, very approximate
C - Development stage - operated on small integrated scale only	3 - Incomplete definition for estimates used
B - Pre-commercial - successful pilot plant operation	2 - Firm basis for values developed
A - Complete - process demonstrated sufficiently to insure commercial success	1 - Values considered to be satisfactory for commercial venture

It is not intended to suggest that these data indicate superiority of any given process. Many situation-specific factors (type of coal, markets served, transportation modes available) will influence process selection for commercial projects. The results do, however, illustrate the potential advantages of applying available technology now.

POTENTIAL MARKETS FOR METHANOL FUEL

Methanol fuels have been demonstrated in a variety of applications:

1. Fuel for motor vehicles, alone, or in combination with gasoline.
2. Fuel for electric utilities, to be burned as supplemental fuel in coal-fired boilers and in combustion turbines.
3. Fuel to replace distillate oil and residual oil being burned in boilers and furnaces for space heat in the residential and commercial sectors.
4. Fuel to replace distillate oil for industrial boilers and direct-fired processes.

FUEL FOR MOTOR VEHICLES

Opinions differ on the ease with which the methanol could be introduced as fuel for motor vehicles. Many believe that methanol could be utilized, with adaptation of the engines, in all types of motor vehicles. Also, many believe that a fuel consisting of up to 10 percent methanol in gasoline could be used in gasoline engines with only minor changes in present practices.[3] Even at the 10 percent level, the market would be significant. Further, even if it is determined that the use of methanol pure or at higher concentrations in gasoline, will require time-consuming adjustments, the feasibility of converting methanol to gasoline with the Mobil-M process could open the way for substituting synthetic fuels for unlimited amounts of our gasoline consumption.

Gasoline consumption in 1980 was 2409×10^6 bbl (12.66×10^{15} Btu).* Ten percent of this total is equivalent to over 60 million tons of methanol. This demand alone would consume the output of eight 25,000-ton/day plants* of the type that has been suggested as an optimum size.[7]

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*All fuel consumption data taken from Reference 13.

FUEL FOR ELECTRIC UTILITY BOILERS

Utilities currently burn a substantial amount of both distillate oil and residual oil; the distillate is used mostly as a supplemental fuel for startup and for flame stability in coal-fired boilers or in oil-fired combustion turbines. Residual oil is burned as a base fuel in large boilers. Methanol has been demonstrated to be applicable as a substitute for both types of fuel and has been used to fire utility boilers. The 1980 consumption of distillate by electric utilities was 39×10^6 bbl (0.22×10^{15} Btu) and their consumption of residual oil was 438 $\times 10^6$ bbl (2.75×10^{15} Btu). Replacement of the distillate with methanol would represent a valuable use as a premium fuel and would consume about 10×10^6 tons per year of methanol at present levels of consumption.

Although methanol could be substituted for residual oil as a base fuel, this probably would not be the best application of a premium fuel in light of other possible uses. Substitution for the portion of residual oil that is imported would operate to reduce dependence on foreign oil. But with refineries worldwide necessarily continuing to produce residual oil (as they will for some years), outlets will be needed. Utilities and industrial combustion may be the most effective way to utilize the residual oil, especially that fraction produced in the United States, which is the dominant portion of that used in this country.

FUEL FOR RESIDENTIAL AND COMMERCIAL SPACE HEAT

The residential and commercial sectors consume large amounts of distillate and residual oil, which is used almost exclusively for space heat and could beneficially be replaced by methanol. Substitution for residual oil in these sectors would offer advantages in that the more complex equipment for burning heavy oil in commercial establishments could be eliminated, air pollution reduced, and dependence on foreign oil reduced. Consumption levels in the residential and commercial sectors in 1980 were distillate, 353 x 10^6 bbl (2.06 x 10^{15} Btu), and residual, 86 x 10^6 bbl (0.54 x 10^{15} Btu). This is equivalent to 150 x 10^6 tons of methanol at present levels of consumption.

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*Assumed to be operated at 90 to 95 percent of capacity.

FUEL FOR INDUSTRIAL BOILERS AND DIRECT-FIRED PROCESSES

Methanol also appears to be a satisfactory substitute for distillate oil in industrial boilers. Distillate oil burned in the industrial sector goes both into boilers and into direct-fired processes such as dryers and kilns. Even though direct-fired processes are highly heterogeneous, it seems reasonable to assume that methanol could be used in almost any situation where distillate is direct-fired. For reasons discussed in connection with utility boilers, the industrial combustion of residual oil is not included as a potential market for methanol fuel, even though it could be used in such applications.

The industrial consumption of distillate oil in 1980 was 257 x 10^6 bbl (1.50 x 10^{15} Btu), the equivalent of 75 x 10^6 tons of methanol.

Table 3 shows a summary of the major applications in which methanol appears to be substitutable.

TABLE 3. SUMMARY OF METHANOL-SUBSTITUTABLE OIL CONSUMPTION (1980)

	Consumption, 10^{15} Btu	Methanol equivalent, 10^6 tons	Oil equivalent, 10^6 bbl
Distillate oil, utility sector	0.22	11	39
Distillate oil, res/comm sectors	2.06	103	353
Residual oil, res/comm sectors	0.54	27	86
Distillate oil, industrial sector	1.50	75	257
Motor gasoline (10%)	1.27	64	241
	5.59	280	976

The total consumption shown in Table 3 amounts to over 15 percent of the total U.S. oil consumption of 34.3×10^{15} Btu in 1980. This figure would be considerably larger if it were assumed that methanol converted to gasoline with the Mobil-M process could be substituted for the entire gasoline consumption of 12.66×10^{15} Btu. Also, amounts for consumption of diesel fuel (2.33×10^{15} Btu in 1979) are not included, even thought it is said to be replaceable with methanol with appropriate engine modifications.

Replacement of the oil products indicated in Table 3 with methanol would require building about thirty-five 25,000-ton/day plants at a cost of about $100 billion. In terms of oil consumption, this comes to a little under 3 million barrels per day, or about 50 percent of our imports. An additional 65 to 70 plants costing around $175 to 200 billion would be required to produce gasoline in amounts equal to 1980 consumption.*

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*Plant sizes assumed and costs estimated are from Reference 7.

PROSPECTS FOR COMMERCIALIZATION OF METHANOL AS FUEL

It is widely accepted that nontechnical problems such as lack of assured markets, unclear policies in regulatory agencies, potential siting difficulties, and related social, economic, and institutional problems are the main barriers to commercialization of methanol fuel or other fuels produced by presently available technologies. Growing pressure for the use of present technology to replace petroleum-derived fuels should alleviate these problems. If it does, the prospects for methanol fuels will depend primarily on advantages they offer over competitive fuels. The following is a discussion of methanol relative to the other fuels that might be produced by present technology to compete, directly or indirectly, with methanol fuels in replacement of petroleum-derived liquid fuels. These are the principal options:

1. Natural gas.
2. Low- or medium-Btu gas made from solid fossil fuels with existing technology.
3. Gasoline derived directly from synthesis gas from coal using Fischer-Tropsch technology.
4. Gasoline produced by subsequent processing of methanol, derived from fossil fuels, using the Mobile-M process.
5. Ethanol produced by fermentation of agricultural crops.
6. Shale oil.

It might be argued that synthetic natural gas (SNG) and fuels produced from direct liquefaction should be considered along with those listed above. They are not, however, because these technologies are not equivalent to the others in terms of stage of development or potential application. Although one SNG plant is reported under construction, this plant will produce supplemental fuel for existing natural gas distribution systems and will not be in direct competition with the fuels being considered. Moreover, the facts do not indicate that direct liquefaction technologies are presently utilizable in the same sense as those used for the above fuels.

METHANOL VERSUS NATURAL GAS

Methanol and natural gas both have potential for replacement of petroleum-derived fuels. Gas can be used directly or as a feedstock for production of methanol. Whether or not natural gas should be used in either way depends on the adequacy of supplies for other critical uses. Until recently the expanded use of natural gas would have been impossible because of short supplies. Since passage of the Natural Gas Policy Act of 1978, which provides for progressive deregulation of natural gas prices, drilling has been increased so that supplies have increased. Although the proven reserves for the lower 48 states were only 195 trillion cubic feed (Tcf) at the end of 1979 (a 10-year supply at 1980 rates of consumption), the total remaining conventional gas resources have been estimated to be 563 to 1219 Tcf.[14] The higher figure is the most recent estimate. In addition, natural gas is known to be recoverable from "unconventional" domestic sources, which include geopressure zones, Western "tight sands", methane from coal seams, and Devonian shales underlying Appalachia.[15,16] Estimates of recoverable natural gas from these resources were recently summarized; these data are presented in Table 4.[16] The wide range of values reflects our present poor understanding of the character of the resources.

TABLE 4. ESTIMATED UNCONVENTIONAL GAS RESOURCES FOR THE UNITED STATES[16]

Resource	Estimated total resource in place, Km^3 (Tcf)	Recoverable resources, Km^3 (Tcf)
Western tight gas sands	1,400-17,000 (49-600)	710-8,860 (25-313)
Eastern devonian gas shales	2,100-20,000 (74-706)	280-14,300 (10-505)
Methane from coal seams	2,000-24,000 (71-847)	450-13,800 (16-487)
Geopressured methane	85,000-1,400,000 (3,000-49,420)	4,200-57,000 (148-2,012)
	90,500-1,461,000 (3,794-51,573)	5,640-93,960 (199-3,317)

In recent months natural gas advocates have argued for "the natural gas option" as a worldwide approach to reducing dependence on oil. They point out that proven worldwide reserves of conventional gas are 2200 Tcf. Estimated remaining undiscovered reserves are said to be 7500 Tcf, giving a total resource that is believed adequate for 50 years even if the present annual worldwide consumption rate of 50 Tcf is doubled.[17] Even if one accepts a lower estimate made in 1975 of 6000 Tcf for total recoverable conventional reserves,[18] the world supplies seem impressive. Utilization of the worldwide gas supplies will, however, require capture of the gas and transport to remote demand points. Some propose that this be accomplished with pipelines and ships transporting liquid natural gas (LNG). Others suggest that where pipelines must be over 5000 miles long or ship transport exceeds 3000 miles, conversion to methanol for shipment is more economical. In addition, the methanol advocates cite the advantages of liquid fuels in markets such as transportation fuels, where natural gas is not widely applicable.[7]

In summary, it appears that natural gas may become increasingly important as a direct substitute for petroleum. At the same time, it also seems appropriate to consider conversion of substantial quantities of natural gas to methanol by present technology to produce direct substitutes for some of the liquid fuels that we are now consuming in amounts equivalent to about 34 x 10^{15} Btu per year. These fuels are now produced partly from domestic oil supplies and partly from about 17 x 10^{15} Btu of imported oil. The magnitude of these numbers is illustrated by comparison with the natural gas consumption for recent years of 20 Tcf/yr, which represents approximately 20 x 10^{15} Btu. No single approach will provide more than a partial solution. Even if the use of natural gas is greatly expanded, there might still be a role for methanol fuels.

METHANOL VERSUS LOW- AND MEDIUM-Btu GAS FROM COAL

Low- and medium-Btu gas can be produced with existing technology and used on-site. Medium-Btu gas, which can be moved by pipeline for short distances, can be produced for use in plants within about 100 miles. Hence, where coal is available near a point of demand, there may be little incentive to produce methanol from coal-derived gas rather than burn the gas directly. Supplies of solid fuel in remote locations, however, might be profitably gasified, converted to methanol, and shipped to distant demand points. This is especially true of low-grade fuels, which are expensive to ship (on a Btu basis) and are more effectively gasified than high-grade coal. Several such plants are being designed to utilize lignite in the United States.[19] Peat, which has little value as fuel except on-site, has also been suggested to be an excellent gasification feedstock. One report indicates that 11,000 and 37,000 square miles of peat bogs with thicknesses of 5 to 25 ft are located in the U.S. and Canada, respectively. The data suggest that the U.S. supply might be equivalent to 6.5 billion tons that could yield about 2.0 billion tons of methanol or 80 x 10^{6} ton/yr for 25 years.[20] This annual amount is over 12 percent of our total gasoline consumption in 1980.

METHANOL VERSUS GASOLINE FROM COAL (FISCHER-TROPSCH)

Production of gasoline from coal by the Fischer-Tropsch process might be an attractive alternative for production of non-imported liquid fuels. This technology has been used for many years in South Africa and is being greatly expanded in new capacity. The process, however, produces a wide variety of products for which markets must be available. Further, the quality of the fuel as produced is low relative to methanol fuel or Mobil-M gasoline. Additional processing is required to produce high-octane gasoline. Also, the Fischer-Tropsch process appears to be relatively lower in efficiency and higher in cost, as discussed earlier, when the value of the products is considered. The process does, however, produce a significant amount of gasoline directly, and unless the Mobil-M process is successful, it will be the only currently available option for doing so.

METHANOL FUEL VERSUS GASOLINE FROM METHANOL (Mobil M-Gasoline)

It may be debatable whether the Mobil-M process can be considered available technology, since no full-scale process is in operaton. It is, however, further along in development than other processes in that a commercial plant is to be built. Some consider that processing of methanol in an additional step, as this process does, is unnecessary because methanol is claimed to be usable in amounts of 10 percent or more with gasoline in motor vehicles of conventional design and to be usable pure in motor vehicles of modified designs. Others argue that this is an oversimplification, claiming that certain properties of methanol, including its corrosiveness, toxicity, and affinity for water, constitute problems that would require time-consuming modifications of present practices if methanol is to be widely used in motor vehicles. The Mobil M-Gasoline process in claimed to have 95.5 percent thermal efficiency in conversion, and is said to add only 5¢ per gallon to the cost of output fuel.[21] If this performance is attainable, the technology could be quite useful in attaining faster penetration for coal-derived fuels in the transportation fuel market.

METHANOL VERSUS ETHANOL FROM FERMENTATION OF CROPS

Ethanol from fermentation of crops is being used as motor fuel both in the United States and abroad. Problems and advantages associated with its use are in many ways similar to those associated with the use of methanol. Ethanol is, however, subject to certain unique limitations, primarily associated with availability of raw materials. Thus, even though ethanol production is a useful technology, it may be more limited in applicability than that for methanol fuels, in the long run.

Ethanol plants are expected to be relatively small so that they can be located near raw material supplies (such as corn) and near outlets for byproduct animal feed, the sale of which is essential to process economics. Also they effectively remove land from food production at a time when there is already concern over the rate at which farm land is being lost to other uses. Experience to date suggests that ethanol will play a role in replacement of petroleum fuels but is not likely to be a dominant contributor.

METHANOL VERSUS FUEL FROM OIL SHALE

Fuels from shale oil, like M-Gasoline, have not been produced commercially, but plans have been made for commercial plants. There is a considerable body of pilot plant data to support the scaleup of oil shale processes. The technical risk for commercial plants appears to be minimal. Further, oil shale deposits are very extensive and could supply our oil needs for hundreds of years. Because of economic uncertainties, however, developers are reluctant to make firm committments without such incentives as guaranteed markets. Hence, prospects are poor for near-term production of large amounts of synfuel from oil shale. Also, crude feedstocks from oil shale are of low quality compared with methanol. Thus, it appears that markets for methanol fuel should exist even if shale oil ventures are highly successful.

CONCLUSIONS

Methanol fuel technology appears to be very cost-competitive with other technologies that could be applied in a synthetic fuels industry today. Although the projected cost of methanol fuels is somewhat higher than today's prices for distillate oil and gasoline, methanol fuel plants built now could prove to be highly profitable at prices that may prevail when they come on stream.

The "clean burning" characteristics of methanol make it potentially attractive from the standpoint of combustion system design and control of environmental impacts associated with its use. Also, methanol is easily transportable and could be produced from abundant supplies of low-grade fossil fuels located in regions of the United States remote from points of demand for premium fuels. Hence, technology for production of methanol could be applied to utilize energy supplies that would otherwise be of limited usefulness.

Methanol fuels seem to be an attractive alternative to premium fuels in several critical applications that are expected to grow in importance. One of the most important involves replacement of gas and distillate oil fired in turbines used by utilities for peaking, in combined cycles, or "repowering" to increase the capacity of existing power plants.

The use of methanol fuel technology to convert natural gas to liquid fuels as a short-term solution for oil shortages should be given serious consideration. Markets in which methanol fuels could be substituted are large and represent a significant portion of our current oil imports. The amounts of natural gas that could be produced over the next 20 years are highly controversial. The optimistic estimates suggest that allocation of significant quantities to production of liquid fuels could be helpful in solution of short-term problems.

A thorough study of possibilities for the use of methanol fuels on a wide scale is needed. Such a study should begin with analysis of gaps in the available information, which has been developed in piecemeal studies conducted over the past 10 to 15 years. This full-scale analysis should lead to definitive conclusions with respect to the policies to be adopted in future energy programs.

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CONVERSION AND EQUIVALENCY FACTORS

1 bbl (barrel) = 42 gallons

1 bbl gasoline = 5.4×10^6 Btu

1 bbl methanol = 2.7×10^6 Btu

1 ton methanol = 20×10^6 Btu

1 ton methanol = 7.4 bbl methanol and is equivalent to 3.7 bbl gasoline

1 Tcf (trillion cubic feet) of natural gas = 10^{15} Btu

1 Km^3 (cubic kilometer) of natural gas = 35.3×10^9 cf (cubic feet)

1 Km^3 of natural gas = 35.3×10^{12} Btu

Density of gasoline = 5.8 lb/gal

Density of methanol = 6.6 lb/gal

A 25,000 ton/day methanol plant produces 8.2×10^6 ton/yr which is equivalent to 30.3×10^6 bbl of gasoline.

Motor gasoline consumption for the U.S. was $2{,}409 \times 10^6$ bbl in 1980. This is equivalent to 12.66×10^{15} Btu. This amounts to 6.3×10^6 bbl/day.

Oil imports for 1980 were 6.8×10^6 bbl/day. This included refined petroleum products amounting to 1.6×10^6 bbl/day (3.2×10^{15} Btu/yr) and crude oil amounting to 5.2×10^6 bbl/day (10.4×10^{15} Btu/yr).

Natural gas consumption in the United States in 1980 was 21.5 Tcf, which is equivalent to 21.5×10^{15} Btu or 10.7×10^6 bbl/day of crude oil.

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METHANOL AS AN ALTERNATIVE TRANSPORTATION FUEL†

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ABSTRACT

Over the remaining years of this century synthetic fuels will play a key role in the nation's drive for energy independence. Although self-reliance is indeed a desirable goal, many people believe it cannot be achieved without significant compromises in environmental quality. This may not be the case. One synfuel, methanol, could be used to replace both gasoline and diesel fuel and yield environmental benefits. This paper compares methanol with synthetic fuels from other coal liquefaction processes in terms of the environmental and economic consequences of their use.

INTRODUCTION

Several factors must be addressed when considering the viability of an alternative motor fuel. These can broadly be grouped into two categories, environmental and economic. Each of these categories would include the production, distribution, and in-use aspects of the fuel in question. In the report that follows, we have attempted to address these issues for several alternative automotive fuels, especially methanol, which could be produced from coal. In addition to methanol from indirect liquefaction, fuels from the following technologies were examined: the Mobil Methanol to Gasoline (MTG) indirect liquefaction process, and the Exxon Donor Solvent (EDS), H-Coal, and Solvent Refined Coal (SRC-II) direct liquefaction processes.

Of the subjects examined below, the environmental analyses of production and distribution are the most general since the least amount of information was available in these areas. Although more detail is provided in other sections, the preliminary nature of the entire report should be emphasized. More work is needed before final conclusions can be stated with confidence.

ENVIRONMENTAL

PRODUCTION AND DISTRIBUTION

It should first be recognized that coal itself contains many diverse elements and compounds in addition to hydrogen and carbon, such as organic nitro-compounds, organic and inorganic sulfur, and trace metals, such as lead, arsenic, etc. The conversion of coal to other fuels offers a number of opportunities for these pollutants to reach the environment in harmful ways, regardless of the particular conversion process used.

One potential advantage of processes which gasify coal, such as those leading to methanol or gasoline (via methanol), is that the gasification itself places most of the potentially harmful elements and compounds into forms which can be removed relatively easily. For example, minerals and heavy metals are removed from the gasifier as slag which cools to a solid. While the high concentration of metals, etc. requires careful disposal, this disposal may not be as difficult as that connected with coal liquefaction. With direct coal liquefaction, these compounds are entrained in the heavy organic liquid and must be separated from the liquid phase later in the process. This solid-liquid separation is very difficult (basic research is still underway in this area[1]) and the separation from a solid cannot be made as completely as the separation from a gas. Inevitably, some liquid will end up with the solid waste and some heavy metals will be left in the crude fuels. Thus, not only may the solid waste disposal problem be worsened by the addition of complex, polycyclic organic material to the waste, but the fuel itself still contains more minerals and heavy metals.

One factor which may mitigate or eliminate this problem for most direct liquefaction processes is the high probability that most of the heaviest liquid fraction will be gasified to produce hydrogen.[2,3] If this is done, most of the minerals and heavy metals can be removed from the gas fairly early, since this heavy liquid fraction should contain most of the coal's impurities. Thus, the full extent of this disadvantage may depend primarily on the fraction of the impurities which can be removed via gasification and the fraction which must be removed directly from the liquid itself.

Another potential advantage of gasification over direct liquefaction is the fact that all of the organic nitrogen and sulfur is broken down to simple compounds like ammonia and hydrogen sulfide. These are relatively easy to separate from the carbon monoxide and hydrogen which make up the major part of the synthesis gas. Also, since the carbon monoxide and hydrogen must be essentially free of nitrogen and sulfur before reacting over the catalyst to form methanol, there is an economic incentive to remove these two elements. Although the nitrogen which is not removed prior to the catalyst will be removed by the catalyst itself, slowly deactivating it, any unremoved sulfur would rapidly deactivate the catalyst.

Coal liquefaction, on the other hand, inherently leaves most of the sulfur and nitrogen in the liquid phase, bound with the organics. The most effective technique to remove these compounds is hydrogenation, which also is used to upgrade the fuel. However, hydrogenation is expensive, because of the large amounts of hydrogen consumed, and will likely be limited to only the degree that is necessary to market the fuel.[4] If the fuel is upgraded to gasoline or high quality No. 2 fuel oil, most of the sulfur and nitrogen will be removed and there should not be any significant problems. However, that portion of the synthetic crude which may be burned with little or no refinement could contain relatively high levels of these elements and represents more of an environmental hazard than gasification products.

The remaining distinct difference between the environmental effects of coal gasification and coal liquefaction processes (prior to end-use) is in exposure to the fuel itself, after production and in distribution. While coal liquids are for the most part hydrocarbons and, as such, are similar to petroleum, they are more aromatic and contain significant quantities of polycyclic and heterocyclic organic compounds. Some of these compounds are definitely mutagenic in bioassays and many have produced tumors in animals. Thus, while the noncarcinogenic health effects of these materials would be more similar to those of crude petroleum, they would definitely have the potential to be more carcinogenic. There is also some evidence that much of this bioactivity can be removed by moderate to severe levels of hydrogenation which would occur if high grade products were produced. Thus, again the potental hazard is dependent upon the degree of hydrogenation given the products.

Indirect liquefaction products, on the other hand, do not appear to exhibit mutagenicity or carcinogenicity. Methanol is neither mutagenic nor carcinogenic and early tests run on M-gasoline have shown it to be nonmutagenic, similar to petroleum-derived gasoline. Therefore, either of these two products offers some degree of benefit over direct liquefaction products. It is possible, however, that methanol produced from coal may contain impurities and that such impurities may affect exhaust products when used. Research needs to be done in this area, also.

Methanol, of course, is highly toxic in heavy exposures, leading to blindness or death. Much of its notoriety in this area is due to people confusing it with ethanol and drinking it in large quantities. Hydrocarbon fuels, while also toxic, do not suffer from this confusion and are not often taken internally. With proper education of the public, confusion between methanol and ethanol should be minimized. However, more work is still needed in this area also.

The final point which deserves mention here is the difference between the effect of an oil spill and a methanol spill. The effects of oil spills are well known; oil films stretching for miles, ruined beaches, surface fires, etc. The effects of a methanol spill are expected to be quite different, primarily because methanol is soluble in water. While high levels of methanol are toxic to fish and fauna, a methanol spill would quickly disperse to nontoxic concentrations and, particularly in water, leave little trace of its presence afterward.[5] Sea life should be able to migrate back quickly and plant life should begin to grow back quickly, though complete renewal would take the time necessary for new plants to grow back. Also, if a methanol fire does start, it can be effectively dispersed with water, which is not possible with an oil fire. However, methanol flames can be invisible, making them more difficult to avoid.

The various relative environmental aspects of synthetic fuels production and use mentioned above are those which appear to stand out at this time. More work, however, is still needed in most areas. Although natural gas to methanol plants exist and have led to much experience in handling methanol, questions related to methanol production from coal are not known with absolute certainty since such large scale facilities do not currently exist. Similarly, no real life experience of the effects of the production of synthetic crudes exists, nor of their use. Given these caveats and the need for further research, however, the indirect liquefaction route to yield methanol or gasoline (from methanol) appears to have some potential environmental advantages over direct liquefaction processes.

VEHICLE USE

The data presented below were obtained from tests of actual methanol engines. However, it should be noted that these data were taken using engines which were only roughly converted to use of methanol; fully optimized engines would be expected to show further improvements in fuel efficiency and emissions.

The worst problem concerning methanol's actual use centers around its low vapor pressure and high heat of vaporization. These properties make it difficult to start a neat methanol engine in cold weather.[6] Also, methanol has a very low cetane number of approximately 3, which means that it is very difficult to ignite in a compression-ignition engine (e.g., a diesel). Problems associated with materials compatibility and lubrication also exist, but these problems already appear to be solvable with existing technology, requiring only that the auto designer know that methanol is going to be the engine fuel.

Various techniques are already being tested which will improve the cold-starting capability of gasoline engines operating on methanol, such as better mechanical fuel atomization, electrical fuel preheating, and the blending of volatile, low boiling point components into the methanol. Methanol's ignition problems are more serious in diesel engines, but several possible solutions are being investigated, such as glow plugs and spark ignition. Brazil already has an experimental methanol-fueled diesel running on the road which uses relatively inexpensive glow plugs as ignition aids and M.A.N. in Germany has designed a diesel bus engine with spark ignition which runs on methanol.[7,7a]

As will be seen later in the section on fuel consumption in the economics section, the fuel properties of methanol which lead to these difficulties also lead to many advantages, such as increased thermal efficiency relative to gasoline engines. Past experience with both gasoline and diesel engines has shown that the disadvantages of a fuel can usually be overcome to allow exploitation of the advantages, particularly when the advantages are as large as they appear to be for methanol.

Methanol engines promise improved emission characteristics over gasoline and diesel engines in a number of areas. Especially important are low emissions of nitrogen oxides (NOx) and an absence of emissions of particulate matter, heavy organics and sulfur-bearing compounds. One possible side benefit of methanol use could be that precious metal catalysts might not be needed for emissions control. Because methanol fuel will contain no sulfur, phosphorus, lead, or other metals, base metal catalysts (e.g., nickel, copper, etc.) may suffice. One likely negative impact of methanol engines would be an increase in engine-out aldehyde emissions, particularly formaldehyde. Catalytic converters, however, would be expected to reduce aldehyde emissions to acceptable levels. The available data supporting these effects are discussed below.

A search of the literature shows a general consensus that methanol engines produce approximately one-half of the NOx emissions of gasoline engines at similar operating conditions, with individual studies showing reductions between 30 percent and 65 percent.[8,9,10,11,12] One of the major engine design changes expected with methanol engines is the use of higher compression ratios to increase engine efficiency. Experiments have confirmed the theoretical expectation that these higher compression ratios, with no other design changes, will increase NOx emissions considerably due to the higher combustion temperatures.[13,14] However, with high compression ratios, less spark timing advance is needed. Retarding spark timing is known to reduce both NOx emissions and engine efficiency. Fortunately, it has been shown that the combination of a much larger compression ratio with a few degrees of spark timing retard can both increase thermal efficiency and decrease NOx emissions.[14] This raises the possibility of methanol vehicles being able to meet the current 1.0 gram per mile NOx emission standard without the need for a NOx reduction catalyst.

Use of methanol in a diesel engine should also reduce NOx emissions by the same degree as that described above. Diesel engines have higher peak combustion temperatures and the effect of a cooler-burning fuel should actually be even more apparent in a diesel than in a gasoline engine. Unfortunately, no data to confirm this is yet available from a diesel engine running on pure methanol. However, emission tests have been performed on a dual-fuel diesel, where a small amount of diesel fuel is injected to initiate combustion of the methanol. These tests have shown NOx emission reductions as high as 50 percent.[15,16]

These lower NOx emissions would aid many areas of the country in attaining the ambient standard for NO_2 in the future. (Most areas are currently under compliance with the NO_2 ambient air quality standard, but many are projected to exceed it in the future as NOx emissions continue to rise.) Lower NOx emissions would also help alleviate the acid rain problem, though the majority of this problem appears to be due to stationary source emissions. Finally, the use of methanol would also provide a method for heavy-duty engines to reduce NOx emissions closer to the congressionally-mandated level without giving up any of the fuel economy advantage of diesels, as will be seen later.

The lack of hard data on diesels operating on pure methanol indicated above will also be evident below as other aspects of methanol-fueled diesel engines are discussed. The basic reason for this lack of data is that until recently methanol has not been seriously considered to be an acceptable fuel for a diesel engine because of its very low cetane number. For many years, studies examining methanol as an engine fuel concentrated on gasoline-type engines (fuel inducted with combustion air). However, as the more recent studies are indicating, it appears possible to burn methanol in a diesel accompanied with some kind of ignition assist and, therefore, utilize the efficiency of the diesel concept.

In addition to the positive effect on NOx emissions, use of methanol engines should provide even greater benefits with respect to emissions of particulate matter and heavy organics from diesels. Gasoline engines operated on unleaded fuel emit only small quantities of particulate matter, composed primarily of sulfate particles. Thus, any improvement in particulate emissions from switching to methanol from gasoline would be small.

However, diesel engines emit large quantities of particulate matter consisting of solid carbonaceous particles (soot) and liquid aerosols. The former are generally formed when the injected fuel droplets are incompletely combusted, leaving carbon particles. These solid particles can then serve as nuclei for more harmful organic species to adsorb onto and as "vehicles" for such compounds to reach (and possibly lodge in) the deep regions of the lung. Although reductions in diesel engine particulate have been reported, particulate matter seems to be an inherent pollutant in diesel-fueled compression ignition engines.

Methanol, on the other hand, is a "light" fuel relative to diesel fuel and should produce far less carbonaceous particles, as do other hydrocarbon fuels "lighter" than diesel fuel. In addition, since methanol does not contain inorganic materials like sulfur or lead, there should not be any other types of solid particulate formed. Accordingly, with pure methanol there would be no nuclei for liquid aerosols to adsorb onto and total particulate emissions would be expected to be near zero. [17] This is certain to be the case with a well designed methanol-fueled spark-ignition engine. [18] Unfortunately, however, we know of no studies which have measured particulate from compression ignition engines burning neat methanol. Several studies (all of which used a small amount of diesel pilot fuel) have reported much lower smoke levels, both in single-cylinder tests and in a 6-cyclinder, turbocharged, direct-injected engine. [7,15,19] There seems to be little question, however, that neat methanol combustion in compression ignition engines would result in very low (and possibly zero) particulate emissions. This would result in a very important environmental advantage compared to diesel fuel combustion.

As mentioned earlier, formaldehyde emissions from methanol engines are of some concern since there is some evidence that formaldehyde is carcinogenic. Formaldehyde is an intermediate specie in methanol oxidation and would be expeced to be emitted from methanol engines in greater quantities than either diesel or gasoline engines. Many studies have shown total aldehyde emissions (mostly formaldehyde) from methanol engines to be two to ten times greater than aldehyde emissions from gasoline engines. [20,21,22,23]

At the same time, catalytic converters have been shown to be effective in removing approximately 90 percent of exhaust aldehydes. [9,10,23,24] Much research has been performed regarding the parameters which influence aldehyde formation in gasoline engines, with low exhaust temperatures and high oxygen concentrations identified as leading to higher formaldehyde formation rates, and this knowledge should facilitate aldehyde control in future engine designs. [22,25] Aldehyde emissions from methanol combustion in diesel engines are also expected to be greater than from diesel fuel combustion.

The last benefit of methanol engines to be discussed concerns sulfur emissions. Because of the way methanol is produced it contains essentially no sulfur. And, if there is no sulfur in the fuel, no emissions of sulfur-bearing compounds, such as sulfur dioxide, sulfuric acid, or hydrogen sulfide, can occur. This is a slight improvement over gasoline emissions, since gasoline does have a small amount of sulfur in it. Catalyst-equipped gasoline engines currently emit between 0.005 and 0.03 grams per mile of sulfate and this would disappear with the use of methanol, even if catalysts were still used.

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The improvement over the diesel, however, would be more pronounced. Diesel fuel currently contains 0.2-0.5 percent sulfur by weight. This translates into about 0.25 grams per mile of elemental sulfur from diesel trucks (0.5 grams per mile of sulfur dioxide, or 0.75 grams per mile of sulfate, equivalent). Diesel cars emit about one-fifth this amount. Since the sulfur level in diesel fuel is expected to rise in the future, these emission levels would also rise in the future. With the use of methanol these emissions would disappear altogether.

ENVIRONMENTAL SUMMARY

Although coal contains many substances which could be environmentally damaging, it appears that indirect liquefaction processes, methanol and Mobil MTG, can facilitate their removal easier than is possible through direct liquefaction routes such as EDS, SRC-II and H-Coal. Further, since indirect liquefaction necessitates the removal of all sulfur before the fuel is synthesized, the use of relatively cheap base metal catalysts (as opposed to noble metals currently in use) on automobiles is a possibility.

Neither methanol nor Mobil M-gasoline appear to exhibit mutagenicity or carcinogenicity. It should be remembered, however, that commercial coal-to-methanol plants are not yet available so the influence of possible impurities is not yet known. Direct coal liquefaction products are more aromatic and contain significant quantities of polycyclic and heterocyclic organic compounds, some of which are mutagenic. There is some evidence, however, that much of this bioactivity can be removed by moderate to severe levels of hydrogenation. More work needs to be done in these areas before definitive conclusions can be reached.

The effects of a methanol spill are expected to be quite different from that of the classical oil spill since methanol is soluble in water. Although high levels of methanol are toxic to fish, a methanol spill should quickly disperse to nontoxic levels.

Methanol engines promise emission benefits over both gasoline and diesel engines. Lower emissions of nitrogen oxides, and the virtual absence of particulate matter, heavy organics and sulfur bearing compounds from vehicle exhaust are promising. A possible detriment of methanol engines is that they emit higher amounts of aldehydes, principally formaldehyde which is carcinogenic. Catalytic converters, however, have been shown to be effective in removing 90 percent of exhaust aldehydes. As was the case with the environmental consequences of synfuel production, more work needs to be done in the vehicle-use area as well.

ECONOMIC

We have analyzed a large number of studies in order to estimate the costs associated with the production and use of synthetic fuels. A superficial review of their conclusions quickly revealed a wide variety of conclusions and recommendations. One reason for this is that the economic bases used by the various studies often differ, affecting costs by as much as 100 percent. Another reason is that each study uses the best information available at the time of the study. Since the product mixes, efficiencies and costs of many of these processes, especially the direct liquefaction processes, change frequently as more is understood about the process, studies performed even 2 or 3 years ago cannot be compared to the latest studies.

Thus, we have attempted to go back in each instance to the original engineering studies to assess the viability of the cost estimates. We also have compared the available designs of each process to ascertain which are out-dated or based on now inaccurate assumptions. After doing this, the projects were placed on the same economic basis and adjusted for plant size.

While the difficulties and apparent discrepancies described above primarily involve the costs of producing synthetic fuels, the overall economic picture involves more. The entire process of producing synthetic fuels and using them in motor vehicles will be broken down into three areas. The first area consists of the production of a usable liquid fuel from raw materials. The second area consists of distribution of this fuel. Finally, the third area includes the use of these fuels in motor vehicles. All costs will be presented in 1981 dollars. It should be noted that the general approach followed in this section is from a long-term perspective. That is, we have not identified any detailed costs associated with the implementation of methanol as a "new" transportation fuel.

PRODUCTION COSTS

Determining the economics of the production of usable synthetic liquid fuels is probably the most difficult of the three areas to be examined. The engineering and financial bases that have been chosen are shown in Tables 1 and 2. As shown in Table 1, two different sets of financial parameters were chosen. These were selected from a survey of recent studies[26,27,28,29, 30,31] done on coal liquefaction processes and represent two extreme cases for capital charge. The low capital charge rate and accompanying parameters were chosen from the ESCOE report[26] while the high capital charge data were taken from the Chevron study.[28] The important factors yielding these two CCRs are also shown in Table 1.

Table 2 shows the remaining input factors. All plants were normalized to 50,000 fuel oil equivalent barrels per calendar day

TABLE 1. COMMON FINANCIAL PARAMETERS

Financial Parameters	Low Cost Case[26]	High Cost Case[28]
Capital Charge Rate, Percent	11.5	30
Debt/Equity Ratio	40/60	0/100
Discounted Cash Flow Rate of Return on Investment, Percent	Not Available	15
Project Life, Yrs.	20	20
Construction Period, Yrs.	4	4
Investment Schedule, %/Yr.	9/25/36/30	10/15/25/50
Plant Start Up Ratios	50, 90, 100...	50/100
Debt Interest, Nominal Rate, Percent	10	-
Investment Tax Credit, %	9	10
Depreciation Method	Sum of Year's Digits	Sum of Year's Digits
Tax Life, Yrs.	15	13

TABLE 2. PROCESS COST INPUTS AND OTHER FACTORS COMMON TO ALL STUDIES

Cost Inputs and Other Factors	Value
Product Yield	50,000 FOEB/CD
Coal	
a) Bituminous	$27.50/ton
b) Subbituminous	$17.00/ton
c) Lignite	$10.00/ton
Operating Costs	
a) Utilities	$0.035/kw-HR
b) Working Capital Interest	6% of working capital per year.
c) Fuel Cost	$35/bbl
Scaling Factors	
a) Capital Costs	0.75
b) Labor Costs	0.20
c) Maintenance, Taxes, Insurance, General	Same percentage of plant investment as specified by each individual study.
d) Coal, Catalysts and Chemicals, Utilities, Fuel, Natural Gas	Amount varies directly proportional to plant size.
By-Product Credit	
a) Sulfur	$50/ton
b) Ammonia	$180/ton
c) Phenol	$112.6/bbl
Contingency factor	15%
Inflation Rate	
a) 1976	5%
b) 1977	6%
c) 1978	7%
d) 1979	9%
e) 1980	9%
Real Cost Increases (%/year)	
a) Fuel Oil	2%
b) Natural Gas	2%
c) Coal	0%

(FOEB/CD)(one FOB equals 5.9 mBtu, higher heating value). The costs selected for bituminous, subbituminous and lignite coals are respectively $27.50, $17.00, and $10.00 per ton. Because capital costs do not usually vary in direct proportion to plant size, a scaling factor (an exponent) is normally used to modify the ratio of plant sizes (by yield). The scaling factor used here was 0.75, which is an average of factors found from various studies.[29,31, 32,33] To adjust labor and supervision costs a scaling factor of 0.2 was used.[26,32] The rest of the operating costs were assumed to vary directly with plant size. The inflation rate for adjusting the costs of studies to $1981 was based on the Chemical Engineering plant cost index.

The product mix expected from each of the various synfuel processes being investigated can be found in Table 3. In order to put the discussion on costs into a more meaningful perspective, several points should be kept in mind. First, indirect liquefaction processes can yield a product mix which is either essentially 100 percent transportation fuel or a 50-50 mix of transportation fuel and SNG. The latter appears to be more efficient and economical for either methanol or MTG-gasoline production, but the cost of producing essentially 100 percent transportation fuel will be used here since the nation's energy shortfalls are primarily in the transportation area. Second, the product mix from direct liquefaction processes depends largely on the degree of refining applied. Each of the direct liquefaction procedures yields some SNG or LPG which can be sold without further processing, while the remainder of the products in most cases must be refined before marketing. This refining adds to the product's cost. Third, the mixes reported in Table 3 were taken from available refining reports. The SRC-II study was based on maximizing gasoline production while the EDS and H-Coal studies also considered No. 2 fuel oil production. Fourth, none of the synfuel processes being examined produce residual oil or diesel fuel. Residual oil could of course be obtained by the direct liquefaction routes simply by applying less refining. However, products from direct liquefaction plants appear to be too high in aromatics to allow economical production of diesel fuel.

Turning once again to Table 3, it can be seen that capital costs range from $2.04 billion to $3.3 billion. The methanol plants tend to have the lowest capital costs ($2.0-2.5 billion), while that of the EDS process is in the same range near the high end. Using the incremental cost of the MTG process, a gasoline-from-coal plant would cost between $2.6 billion and $3.1 billion. The H-Coal and SRC-II processes are next at $3.3 billion. (The capital costs do not include refinery costs since it is unlikely that new refineries would be built.)

A product value approach was utilized to estimate costs for individual products. This technique assumes that the future prices of particular fuels will maintain a certain relationship, based on relative demand. All prices are normalized relative to a reference pro-

TABLE 3. PRODUCT AND CAPITAL COSTS OF SELECTED COAL LIQUEFACTION PROCESSES (1981 DOLLARS)

Process	Product Mix	Refined Product Cost ($/mBtu)		Capital Cost* (Billions of Dollars)
		11.5% CCR	30% CCR	
Direct Liquefaction				
EDS (Bituminous)	32.7% Reg. Gasoline	10.11	16.57	2.50
	14.0% Prem. Gasoline	10.87	17.81	
	25.6% No. 2 Fuel Oil	8.29	13.59	
	9.6% LPG	7.78	12.76	
	18.1% SNG	8.09	13.26	
H-Coal (Bituminous)	50.7% Reg. Gasoline	8.41	16.13	3.30
	11.0% Prem. Gasoline	9.04	17.34	
	20.1% No. 2 Fuel Oil	6.90	13.23	
	18.2% LPG	6.48	12.42	
SRC-II (Bituminous)	64.7% Gasoline	9.87	19.06	3.30
	12.1% LPG	7.60	14.68	
	23.2% SNG	7.90	15.24	
Indirect Liquefaction				
Texaco (Bituminous)	100% MeOH**	5.90- 6.16	9.80- 10.00	2.06
Koppers (Bitum.)	100% MeOH**	6.97	11.73	2.51
Lurgi (Subbit.)	47.9% MeOH**	5.82	10.02	2.32
	49.7% SNG	6.03	10.55	
	2.4% Gasoline	7.54	13.19	
Modified Winkler (Lignite)	100% MeOH**	5.25	9.12	2.04
Lurgi Mobil MTG (Subbit.)	41.2% Reg. Gasoline	7.54	13.19	2.92
	53.3% SNG	6.03	10.55	
	5.5% LPG	5.80	10.16	
Mobil MTG Incremental Cost	85-90% Reg. Gasoline 10-15% LPG	1.72	3.17	0.6

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* Capital costs are instantaneous costs. Capital costs do not include refinery capital costs.

** MeOH = 95-98% methanol, 1-3% water, and the remainder higher alcohols.

duct, which here was chosen to be gasoline. In this report, a relationship between various fuels similar to that reported in the ICF report was used and is as follows:

1. If the cost of unleaded regular gasoline is $G/mBtu,
2. The cost of No. 2 fuel oil is (0.82)(G)/mBtu, and
3. The cost of LPG is (0.77)(G)/mBtu.[29]

Since unleaded premium gasoline is produced in some cases (EDS and H-Coal), a relationship between this fuel and regular gasoline is also necessary. Unfortunately, a history of the relationship between these two fuels was not readily available. The cost ratio of leaded premium to leaded regular gasoline was used instead. This relationship indicated a cost ratio of 1.075.[34] This product cost relationship was then applied to premium and regular unleaded gasoline.

The cost for SNG was assumed to be (0.8)(G). This value was obtained by averaging those for No. 2 fuel oil and LPG since SNG should share markets with each, especially No. 2 fuel oil.

The product costs, along with capital costs discussed earlier, are shown in Table 3. As can be seen, they follow a similar pattern as capital costs, though not exactly. Speaking first of the low cost scenario, methanol is the cheapest product, ranging from $5.25-$6.97 per million Btu (mBtu) for fully commercial gasifiers and $5.90-$6.16 per mBtu for the near commercial Texaco gasifier. Gasoline via the Mobil MTG process would be $1.72 per mBtu more, or $6.97-$7.69 per mBtu using fully commercial gasifiers and $7.62-$7.84 per mBtu with the Texaco gasifier. H-Coal gasoline costs slightly more at $8.41 per mBtu, while SRC-II gasoline is projected to cost $9.87 per mBtu. Finally, EDS gasoline is projected to cost the most of the automotive products at $10.11 per mBtu.

A similar order holds for the higher cost scenario. In this case, SRC-II has replaced EDS as the process yielding the highest cost product. This is primarily due to the higher capital costs involved for SRC-II. It should also be noted that the absolute difference between methanol costs and the cost of gasoline from the other processes increases because the capital cost of the methanol plant is lower. The same is true for MTG gasoline in most cases. A large change occurs in the difference between EDS and H-Coal process costs. While the EDS costs were 20 percent higher using the low CCR, they are less than 3 percent higher using the high CCR.

Using all the studies which are publicly available, it would generally appear that the indirect coal liquefaction processes can produce usable fuel cheaper than the direct liquefaction technologies.

DISTRIBUTION COSTS

Since distribution systems already exist for gasoline, the economics in this area would, of course, favor the continued use of this fuel over the introduction of methanol. In addition, gasoline also has the advantage of possessing a higher energy density: 115,400 Btu/gal for gasoline compared with 56,560 Btu/gal for methanol. Thus, because transportation costs depend primarily on volume, gasoline would necessarily be less expensive to transport per Btu.

The costs of distributing a fuel can most easily be divided into three areas; 1) distribution from refinery or plantgate (if no refining is required) to the regional distributor, 2) distribution from the regional distributor to the retailer, and 3) distribution by the retailer (i.e., the gas station). These three aspects of distribution will be discussed below.

More detail could of course be added to this analysis to improve the resulting estimates but such information has not yet been assimilated. However, the general conclusions reached below should not change substantially.

To simplify the presentation here, long-range distribution is approximated by that of pipeline transport to a distance of roughly 650 miles.[29] It should be noted that if pipelines are needed to connect coal fields (where synfuel plants are likely to be located) with major markets, then the total costs will be roughly the same whether the plant produces methanol or synthetic gasoline. This is evident since the pipeline must be built in either case and the construction and operating costs increase only slightly with a doubling in size. Further, right-of-way and engineering costs should not change at all with capacity in this range.

In the case of distributing methanol, the total amount of energy distributed would only be about 80 percent that of gasoline due to vehicle efficiency improvements which will be discussed later. However, a gallon of methanol only contains half the energy contained in a gallon of gasoline, so 60 percent more volume of methanol would need to be transported than that of gasoline.

To determine the potential range of the cost of transporting methanol, two bracketing assumptions can be made. One, the cost of transport per volume of fuel can be assumed to remain constant. Two, total distribution costs can be assumed to remain constant. With the first assumption, the estimated cost for gasoline transportation is $0.22 per mBtu.[29] Methanol transportation would cost twice this amount or $0.44 per mBtu. Using the second assumption, where total costs remain constant, the cost for methanol would be $0.27 per mBtu, since only 80 percent as much energy is being transported. Thus, the cost of long-range distribution of methanol is $0.27-0.44 per mBtu.

The costs involved with a switch to methanol will be more related to the increase in volumetric capacity than differences in chemical properties. Pipelines and pumps are almost entirely made from steel or brass, with which methanol is compatible. Rubber seals on pumps may need to be replaced with more durable rubber compounds, but this should be a minor cost.

As mentioned earlier, the next step of local distribution consists of storing fuel at the regional distributor and transporting it to the retailers. This distribution is primarily done by tanker truck and is estimated to cost just over $0.05 per gallon of gasoline, or $0.46 per mBtu. If one conservatively assumes that the cost per volume remains constant, the $0.46 per mBtu cost for gasoline would translate into a $0.92 per mBtu cost for methanol.

Here the cost of conversion to methanol should be very small, even negligible. The only change required should be new rubber seals and hoses, if they were not already made from a material compatible with methanol.

The costs of retailing fuel (the last step) are more like that of long-range distribution than local distribution. The costs of retailing are primarily fixed costs, such as land or rent. Retailing differs from both long-range and local distribution, however, in that fuel energy is the critical marketing factor, not volume.

Typical retailer mark-ups are estimated to be in the range of $0.05-0.18 per gallon of gasoline.[35] However, since the lower mark-ups are usually associated with the high-volume stations, the average mark-up per gallon of gasoline sold in the U.S. should be somewhere between $0.09-0.11, or $0.76-0.95 per mBtu. For methanol, the cost would lie between this range and 25 percent more since the total amount of energy distributed would be 20 percent less. Thus, the cost of retailing methanol would be $0.76-1.19 per mBtu.

In deriving these retail costs, no attempt was made to account for any additional costs the retailer would bear when methanol is first introduced. For example, he will have to make some monetary allowance for the initial small volume of customers. The retailers in some instances will also incur costs associated with installing new tanks if the existing ones are incompatible or unavailable due to large demands for the specific fuels they contain. The abovementioned retailing costs should therefore be considered as long-term costs, after the methanol market stabilizes.

The total cost of distributing methanol and gasoline can now be calculated by simply combining the costs presented in the last three sections. Methanol would cost $1.95-2.55 per mBtu to distribute; gasoline would cost $1.44-1.63 per mBtu. Gasoline has a significant advantage over methanol in terms of percentage (26-36 percent lower), but the absolute difference is only $0.51-0.92 per mBtu.

IN-USE COSTS

In order to determine in-use costs associated with methanol, it is necessary to know its fuel efficiency characteristics. There is general agreement among researchers that methanol is a more energy efficient vehicle fuel than gasoline. There are at least two theoretical reasons why this is so. One, methanol's lower flame temperature reduces the amount of heat transfer from the combustion chamber to the vehicle coolant system. Two, its high heat of vaporization acts as an internal coolant and reduces the mixture temperature during the compression stroke. These characteristics are realized in experiments without having to make any major design changes in current gasoline engines. Studies have shown these inherent properties of methanol to increase the energy efficiency of a passenger vehicle by 3 to 10 percent with a middle range of about 5 percent.[9,12,13]

Other properties of neat methanol combustion allow even greater efficiency improvements. Its wider flammability limits and higher flame speeds relative to gasoline allow methanol to be combusted at leaner conditions while still providing good engine performance. This lean burning capability decreases the peak flame temperature even further and allows more complete combustion, improving energy efficiency. Early testing on a single-cylinder engine yielded estimated energy efficiency improvements of 10 percent due to leaning of the methanol mixture as compared to gasoline tests.[36] Subsequent vehicle testing has shown relative efficiency improvements of lean methanol combustion of 6 to 14 percent.[8,9] Given these results, it would appear that methanol's lean burning capability yields approximately a 10 percent efficiency improvement over and above the 3-10 percent improvement mentioned above. Of course, stratified charge engines have been developed to allow leaner combuction of gasoline as well, and this efficiency advantage of methanol would be lessened with respect to a stratified charge engine.

Methanol's higher octane number also allows the usage of higher compression ratios with correspondingly higher thermal efficiencies. Early single-cylinder testing have estimated the thermal energy efficiency improvements of the higher compression ratios to be in the range of 16 to 20 percent.[14,36] Unfortunately, little vehicle data exist to confirm these figures, but it must be expected that improvements of at least 10 to 15 percent are likely.

Adding up the possible improvements indicates that methanol engines may well be 25 to 30 percent more energy efficient than their gasoline counterparts when the methanol engine is designed specifically for methanol.

However, since such methanol engines are not available for mass distribution today, this section will use a more conservative fuel efficiency advantage for methanol engines over their gasoline counterparts of 20 percent. Using a fuel economy of 30 miles per gallon for the average gasoline-fueled vehicle, this average vehicle would require about 0.0038 mBtu per mile to operate. A methanol-fueled vehicle would be expected to use at least 20 percent less energy or about 0.0030 mBtu per mile.

Using 12,000 miles per year and the average delivered fuel costs, calculated by combining production and distribution costs, the annual fuel savings relative to gasoline produced via indirect liquefaction (Mobil MTG process) were determined (see Table 4). These savings include two separate effects. One, they include the effect of differences in at-the-pump fuel costs. Two, they also include the effect of methanol engines being more fuel efficient than gasoline engines. For consistency, all fuels were assumed to be derived from bituminous coal.

Following this procedure and using the lowest fuel cost (based on the low CCR) and the highest fuel cost (based on a 30 percent CCR), methanol would produce a savings of $131-240 per year compared to gasoline from the Mobil MTG process. Direct liquefaction gasoline would cost an extra $36-410 per year over MTG gasoline, because of its potentially higher at-the-pump cost.

To this fuel savings must be added any difference in engine or vehicle cost. While a methanol-fueled diesel engine may be developed with a fuel efficiency advantage comparable to that of a standard diesel, the conservative 20 percent efficiency advantage over the gasoline engine should be attainable with engines similar to the gasoline engine in terms of both design and cost. While a larger fuel tank and a special cold start system may increase costs, savings should be attained with respect to emission control, particularly if NOx reduction catalysts are no longer needed and if base metal oxidation catalysts can be used instead of platinum and paladium. Thus, whether a methanol engine will cost more or less than a gasoline engine in the long run is still an open question at this time. It would be rather safe to project, however, that any potential extra cost would not override the kind of fuel efficiency benefit described earlier.

ECONOMICS SUMMARY

The results of the past three sections are shown in Table 4. As can be seen when the results are combined, methanol compares favorably to the other fuels. With respect to synthetic gasoline, methanol appears to cost less at the plant gate. This is true whether the low CCR is used or the high CCR. Higher distribution costs lower the difference, but even after distribution, methanol appears to still hold some advantage. This advantage is $1.21- $2.25 per mBtu over MTG gasoline and $2.00-$6.41 per mBtu over direct liquefaction gasoline. For vehicles driven 12,000 miles per year and achieving 30 miles per

TABLE 4. SYNTHETIC FUEL COSTS ($ per mBtu)*

	Indirect Coal Liquefaction		Direct Coal Liquefaction
	Methanol	Gasoline	Gasoline
Production			
Plantgate Cost	5.90-11.73	7.62-14.90	8.41-19.06
Distribution			
Long-Range	0.27-0.44	0.22	0.22
Local	0.92	0.46	0.46
Retail	0.76-1.19	0.76-0.95	0.76-0.95
Cost at Pump	7.85-14.28	9.06-16.53	9.85-20.69
ANNUAL FUEL SAVINGS (RELATIVE TO GASOLINE AT $9.06-16.53 per MBtu)**			
	$131-240	$0	$-(36-189)
ADDED ENGINE COST OVER GASOLINE ENGINE			
	0	0	0

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* Range of plantgate cost is the lowest cost using the low CCR and the highest cost using the high CCR for bituminous feedstocks.

** Includes effect of increased engine efficiences and differences in at-the-pump fuel costs.

gallon (gasoline), methanol would save $131-$240 per year over MTG gasoline and $167-$429 per year over direct liquefaction gasoline if allowances are made for the increased efficiency of methanol engines. Without including the improved engine efficiency, annual savings would be $55-$103 relative to MTG gasoline and $91-292 over direct liquefaction gasoline.

It should be stated that no comparison was made between methanol and diesel fuel since none of the coal conversion processes examined produces diesel fuel of sufficient quality for today's diesel engines. All of these economic results are of course subject to the qualifications which have been stated previously; the primary ones being that the detail of the engineering designs could not be compared across processes, and that cost estimates reflect different points of development for different synfuels.

CONCLUDING STATEMENT

Looking back over the topics addressed in this paper, it can be concluded that at this point in time methanol appears to have environmental and economic advantages over other synthetic transportation fuels derived from coal. The ultimate viability of this conclusion depends on a number of key events or findings. One, a cost-competitive methanol engine must be able to meet the driveability needs of most of the U.S. (e.g., cold-starting in nearly all climates). Two, aldehyde emissions must be controllable at low cost. Three, no other unique and uncontrollable environmental problems of methanol use or production are discovered. Four, the production and distribution cost comparisons made here must hold up against future scrutiny.

The probability of these events occurring can only be estimated by a review of the support for each presented in this study. At this time, we believe the evidence available suggests that the benefits of methanol outweigh its costs.

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PROJECT SUMMARY

A COMPENDIUM OF SYNFUEL END USE TESTING PROGRAMS†

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ABSTRACT

A "Compendium of Synfuel End Use Testing Programs", which provides information on major recently-completed, current and planned synfuel end use testing projects, has been developed. The compendium is intended to promote flow of information among various synfuel testing programs, thereby reducing chances for duplication of effort and enabling design and implementation of cost-effective and systematic approaches to the collection of appropriate environmental data in conjunction with ongoing and planned performance testing projects. It is EPA's intention to update this compendium to include results from current and future testing programs.

Projects described in the compendium involve testing of shale-derived fuels, SRC-II middle distillates, EDS fuel oils, H-coal liquids and methanol-indolene mixtures in various equipment such as utility boilers, steam generators, diesel engines (lab-scale and full-scale), auto engines, and various other combustors. Published reports on various testing efforts and discussions with test sponsors/contractors are the sources of data for the compendium.

Based on the data presented in this compendium, the thrust of the synfuel testing program which has been carried out to date has been to assess equipment performance and fuel handling characteristics. Where some emissions monitoring has been conducted, such efforts have been limited in scope and have primarily emphasized measurement of criteria pollutants (NO_x, SO_x, particulates, etc.). Essentially no data have been collected on emissions of non-criteria/non-regulated pollutants.

INTRODUCTION AND OBJECTIVES OF THE COMPENDIUM

A recently-completed synfuel utilization background study* identified a great need for better coordination among various agencies involved in synfuel end use testing programs so as to promote more systematic approaches to the collection of environmental data in connection with such programs and to reduce chances for duplication of effort. Per recommendation of the background study, a compendium of synfuel end use testing programs has been developed as an information source on major recently completed, ongoing, and planned synfuel end use testing programs. The dissemination of the document among agencies/organizations engaged in various aspects of synfuel production, testing, utilization, and regulation, coupled with holding regular symposia/workshops on synfuel utilization and end use testing, should greatly enhance coordination and flow of information among various programs and, in the long run, contribute to the goal of more rapid establishment of an environmentally acceptable commercial synfuel industry in the U.S. EPA plans to periodically update this compendium to include results from current and future testing programs.

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*M. Ghassemi and R. Iyer, "Environmental Aspects of Synfuel Utilization", EPA Report No. EPA-600/7-81-025, March 1981. (Note: For a summary of this report, see Environmental Science and Technology, Volume 15, No. 8, August 1981, pp. 866-873.)

DATA BASE USED AND DATA PRESENTATION

Information presented on the synfuel testing programs has been obtained from published documents and via telephone calls and/or interviews with organizations involved in the testing programs. The key individuals/agencies providing most of the reports and data used in the compendium are listed in Table 1.

A separate "data sheet" has been devoted to each project covered in this compendium to permit periodic updating of the document to include additional projects and incorporation of further results from ongoing studies. The data sheets are grouped into four categories, covering projects for which the key sponsors/participants are Electric Power Research Institute (EPRI), Department of Defense (DOD), Department of Energy (DOE), and Miscellaneous agencies (e.g., EPA). Data sheets are presented for a total of 44 projects, of which 7 are in the EPRI-sponsored category, 15 in the DOD category, 13 in the DOE category, and 9 in the Miscellaneous category.

Where data have been available, each data sheet provides the following information on a test project: type of fuel tested (both synfuel and the reference petrofuel, where indicated), test equipment used, test site, test objectives, sponsoring agency, contractor, test conditions, environmental monitoring, project status, summary of results, and references (where a report or reports have been published on a project).

A summary of the data contained in the data sheets is presented in Table 2. Tables 3 and 4 present brief descriptions of some of the recently initiated and tentatively planned synfuel testing programs. Two examples of the data sheets are presented.

OVERVIEW OF SYNFUEL TESTING PROGRAMS

Based on the data presented in the test program data sheets and summarized in Table 2, and on the discussions which have been held with a number of synfuel developers, trade associations and potential major users of synfuels,

TABLE 1. LIST OF ORGANIZATIONS/INDIVIDUALS PROVIDING INFORMATION USED IN THE DEVELOPMENT OF THE COMPENDIUM

Electric Power Research Institute
3412 Hillview Drive
Palo Alto, CA 94303
Mr. Al Dolbec

Air Force Wright Aeronautical
Laboratory, Aero Propulsion Laboratory
Wright-Patterson AFB/POSF
Dayton, Ohio 45433
Mr. Charles Delaney

Navy Air Propulsion Center
P. O. Box 7176
Trenton, NJ 08628
Mr. C. J. Nowack

David W. Taylor Naval Ship R&D Center
Code 2705
Annapolis, MD 21402
Mr. Carl A. Hershner

Army Mobility Equipment Research and
Command Center - Attn: DRDME-GL
Ft. Belvoir, VA 22060
Mr. F. Schaekel

U.S. Air Force HQ AFESC/RDV
Tyndall AFB
Tyndall, FL 32403
Major J. Tom Slankas

DOE, Bartlesville Energy
Technology Center
P. O. Box 1398
Bartlesville, OK 74003
Mr. Dan Gurney

DOE, Conservation and Solar Energy Div.
Washington, D.C.
Mr. Gene Ecklund

DOE, Office of Coal Utilization
Fossil Energy Research Center
Germantown, MD
Mr. John Fairbanks

DOE, Laramie Energy Technology Center
P. O. Box 3395
Laramie, WY 82071
Dr. R. Poulson

DOE, Pittsburgh Energy Technology
Center, Analytical Chemistry Division
Pittsburgh, CA
Mr. Curt White

National Aeronautics and Space
Administration, Lewis Research Center
21000 Brook Park Drive
Cleveland, OH 44135
Mr. Rick Niedzwiecki

EPA, Special Studies Branch
Industrial Environmental Research Lab.
Research Triangle Park, N.C. 27711
Mr. G. Blair Martin

EPA, Motor Vehicle Emission Laboratory
2625 Plymouth Road
Ann Arbor, MI
Mr. Robert Garbe

EPA, Combustion Research Branch
Industrial Environmental Research Lab.
Research Triangle Park, N.C. 27711
Mr. G. Blair Martin

EPA, Office of Environmental
Engineering and Technology
Industrial Environmental Research Lab.
Research Triangle Park, N.C. 27711
Mr. W. S. Lanier

EPA, Mobile Sources Laboratory
Research Triangle Park, N.C.
Mr. Frank Black

Southwest Research Institute
Automotive Research Division
6220 Culebra Road
San Antonio, TX 78284
Mr. Charles T. Hare

Southwest Research Institute
Mobile Energy Division
6220 Culebra Road
San Antonio, TX 78284
Mr. John A. Russell

U.S. Department of Transportation
Systems Center
Kendall Square
Cambridge, MA 02142
Mr. Joe Sturm

U.S. Department of Energy and
Coordinating Research Council
Atlanta, GA
Mr. Al Zingle

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Bank of America
4117 Robertson Boulevard
Alexandria, VA 22309
Mr. Gavin McGurdy

Energy and Environmental Research
Corporation
8001 Irvine Boulevard
Santa Ana, CA 92705
Mr. Dave Pershing

Ford Motor Company
Scientific Research Laboratory
Dearborn, MI

Vulcan Cincinnati, Inc.
Cincinnati, OH
Mr. R. W. Duhl

TABLE 2. SYNFUELS-COMBUSTION SYSTEM COMBINATIONS TESTED AND EMISSIONS MONITORED

Test No.	Agency	Synfuel	Reference Fuel	Combustion System	Emissions Monitored	General Conclusions
1	EPRI	SRC-II fuel oil	No. 6 fuel oil	Tangentially-fired utility boiler	NO_x, CO, THC, SO_3, POM, particulates, particle size, particulate composition	• No adverse boiler performance effects with SRC-II fuel. • NO_x emissions nominally 70% higher than No. 6 fuel.
2	EPRI	SRC-II fuel oil H-Coal EDS oil	No. 6 and No. 2 fuel oils	Scaled-down utility boiler	NO, CO_2, CO, SO_2, SO_3, THC, smoke, particulates, particle size	• Higher fuel nitrogen content of SRC-II fuels produced higher NO emissions than reference fuels. • NO emissions from H-Coal and EDS liquids were lower than SRC-II. • No unique differences in combustion or emission characteristics of SRC-II fuel blends.
3	EPRI	SRC-II fuel oil	No. 2 and No. 5 fuel oil	Babcock & Wilcox package boiler	NO_x, CO, CO_2, SO_2, hydrocarbons, O_2, and dust	• NO_x emissions consistent with fuel nitrogen content. • Combustion performance of SRC-II fuel oil was similar to No. 2 and No. 5 fuel oils.
4	EPRI	SRC-II, H-Coal	No. 2 diesel fuel	Three catalytic reactors	NO_x and CO	• Coal-derived liquids can be burned catalytically but SRC-II, and to a lesser degree H-Coal, appeared to degrade reactor performance significantly as evidenced by higher CO emissions. • NO_x emissions were consistent with fuel nitrogen content.
5	EPRI	Hydrogenated shale oil and various liquid fuels for SRC-I, H-Coal, EDS, and SRC-II	No. 2 distillate fuel	Full-scale and sub-scale turbine combustors	NO_x, CO, UHC, particulates, and smoke	• A selected number of coal liquids and shale oil fuels can be used in current turbines. • Emission levels of CO, UHC, and particulates for synfuels were about the same as for No. 2 fuel - not significant. • Significant quantities of FBN are converted to NO_x causing emissions higher than EPA limits.
6	EPRI	Solvent refined coal	Bituminous coal	Utility boiler	NO_x, SO_2, CO_2, particulates, particulate composition	• The boiler stayed much cleaner with SRC than with coal, producing an equivalent boiler efficiency as coal at full load. • The quantity of SRC flyash was 10 to 15% of that of coal flyash with no bottom ash accumulation from SRC. • Particulates, SO_2 and NO_x emissions from SRC were all under EPA limits.
7	EPRI	*	Jet-A fuel, natural gas, methanol	Two utility gas turbines	NO_x, CO, SO_2, THC, POM, sulfates, particulates, aldehydes, opacity	• Methanol is a suitable fuel for gas turbines; turbine performance and NO_x and particulate emissions are improved over the other fuels.

(Continued)

TABLE 2. (Continued)

Test No.	Agency	Synfuel	Reference Fuel	Combustion System	Emissions Monitored	General Conclusions
8	DOD	Shale-derived JP-5 and blends with petroleum JP-5	Petroleum JP-5	DOD helicopter engine: Allison T63-A-5A turboshaft	NO_x, CO, CO_2, and THC	• NO_x emissions increased with increasing fuel nitrogen content; conversion efficiency was about 45%. • No significant effects were noted on engine performance or CO, CO_2, and THC emissions due to the presence of high levels of fuel bound nitrogen.
9	DOD	Shale-derived DFM	Petroleum diesel fuel (MIL-F-16884G)	U.S. Navy LM2500 turbine engine	NO_x, CO, THC, and smoke	• Combustor and engine operating characteristics were identical when using marine diesel or DFM shale oil; thus, DFM shale oil would be suitable for use in LM2500 engines. • NO_x emissions followed fuel nitrogen content; CO and THC levels were essentially the same for both fuels.
10	DOD	JP-5 from oil shale, coal, and tar sands	Jet-A, JP-5, diesel marine fuel, leaded gasoline, and blends of the above	Two high temperature/pressure research combustors	NO_x, CO, UHC, and smoke	• In all performance areas, the synfuels correlated in the same manner as petroleum-derived fuels except for NO_x emissions from the shale oil fuel. • Smoke formation was dependent on hydrogen content; combustion efficiency, CO, and UHC depend more on higher boiling point components than fuel viscosity.
11	DOD	Shale fuel oil	Petroleum diesel fuel marine (DFM)	Steam generator diesel engine	Particulates and particulate composition	• No significant differences between particulate emission products measured in the study from the combustion of DFM or shale fuel oil.
12	DOD	Shale-derived diesel fuel	Petroleum distillate	Lab-scale diesel engine	NO_x, THC, and smoke	• There was no significant difference in performance or emissions with the shale-derived fuel.
13-15	DOD	Shale-derived DFM	Petroleum DFM	3 different types of prototype steam generators	NO_x, SO_2, CO, CO_2, THC, O_2, and smoke	• There were no significant differences in measured pollutant emissions resulting from the combustion of petroleum DFM or shale-derived DFM on the CVA-60, DDG-15, and the FF-1040 boilers. In each case, SO_2, NO_x, and smoke were below levels set by EPA.
16	DOD	Oil shale-derived JP-5 fuel	Petroleum-derived JP-5 fuel	DOD helicopter engine: Allison T62-A-5A turboshaft	NO_x, CO, and THC	• Performance, CO, and THC emissions were equivalent for both fuels. • NO_x emissions followed fuel nitrogen content.

(Continued)

TABLE 2. (Continued)

Test No.	Agency	Synfuel	Reference Fuel	Combustion System	Emissions Monitored	General Conclusions
17	DOD	Unifined kerosene derived from tar sands	Petroleum-derived JP-5 fuel	DOD helicopter engine: Allison T63-A-5A turboshaft	NO_x, CO, and UHC	• Unifined Kerosene was a satisfactory substitute for petroleum JP-5 fuel. • NO_x emissions were slightly higher when using unifined kerosene than with JP-5.
18	DOD	Distillate, aviation, turbine, and diesel fuels derived from coal, tar sands and oil shale	Various petroleum-derived fuels	Wide variety of Army power-plant systems	Various pollutants	• Product quality of many synfuels tested and other results are described in individual abstracts.
19-21	DOD	*	13 petroleum derived fuels: JP-4, JP-8, diesel No. 2 & various blends	General Electric F101 turbofan, J79-17C turbojet, and J79 turbojet engines	NO_x, CO, UHC, and smoke	• In all three engines, fuel hydrogen content strongly affected smoke and NO_x emissions. NO_x emissions were also highly dependent upon combustor operating conditions.
22	DOD	*	12 petroleum-derived fuels: JP-4, JP-8, and various blends	TF41 turbofan combustor	NO_x, CO, UHC, and smoke	• All pollutant emissions measured were highly dependent upon operating conditions. CO and smoke levels were also strongly affected by hydrogen and aromatic content of fuels.
23	DOE	SRC-II middle distillate	Low quality residual oil, and petroleum reference distillate fuel	Combustor sized for use with industrial gas turbine	NO_x, CO, CO_2, THC, and smoke	• The combustor was able to achieve low NO_x with all fuels. • CO and smoke varied directly with rich zone equivalence ratio and inverseiy with lean zone equivalence ratio.
24	DOE	SRC-II middle distillate	Petroleum distillate	Various combustor concepts	NO_x, smoke	• Values of NO_x were reduced for the smaller diameter quench zone and increased for larger diameter quench zone. • Rich-lean burn stage combustion system can meet EPA emission standards.
25	DOE	SRC-II middle distillate	Low quality residual oil and distillate fuel	Seven combustors of varying designs for use in utility gas turbine engines	NO_x, smoke, CO, unburned HC	• A lean-lean combustor has potential for achieving ultra-low NO_x emissions with distillate, residual or other fuels containing up to 0.25% (wt.) fuel nitrogen. CO and smoke met program goals from this combustor also.
26	DOE	SRC-II middle distillate	Low quality residual oil, petroleum reference distillate oil, and natural gas	Combustors for use in utility gas turbine engines	NO_x, CO, THC, smoke	• Lean-lean combustor NO_x emission levels were higher than emission goals using SRC-II fuel. CO emissions remained low using SRC-II fuel, while no smoke was detectable and UHC levels were negligible throughout these tests. • Rich-lean combustor NO_x emissions appeared to reach a minimum below the NO_x emission goal for rich primary zone condition.

(Continued)

TABLE 2. (Continued)

Test No.	Agency	Synfuel	Reference Fuel	Combustion System	Emissions Monitored	General Conclusions
27	DOE	SRC-II middle distillate	Low quality residual oil, petroleum reference distillate oil	Experimental combustor for use with utility gas turbine engines	NO_x, CO, UHC, smoke	• Five combustors have been found adequate for further development: rich-lean diffusion flame venturi quench, burner ceramic lined pipe lean burner, multiannular swirl burner, Rolls-Royce combustor, and lean catalytic combustor. These meet NO_x emission limits set by EPA with petroleum distillate and/or residual oils. • SRC-II fuel NO_x emissions were close to meeting EPA limits in only two combustors: rich-lean diffusion and ceramic lined pipe lean burners.
28	DOE	SRC-II middle and heavy distillate, fuel oils & three blends of the above	No. 2 and No. 6 petroleum-based fuel oils	A 20-hp Johnston, fire-tube boiler	NO_x, SO_2, CO, HC and polynuclear aromatic hydrocarbons	• The levels of NO_x and SO_2 produced were proportional to the amount of nitrogen and sulfur in the fuel. • There appear to be two sources of trace organics in the exhaust gases: small amounts of the fuel itself not burned during combustion, and the products of combustion. For the petroleum fuels, n-alkanes and polynuclear aromatic hydrocarbons are seen in the exhaust gas; for the SRC-II fuels, the alkanes are absent or present at very low levels, and polynuclear aromatic hydrocarbons not seen in the petroleum exhaust gases are present.
29	DOE	*	Indolene and 10% methanol/90% indolene	Two light duty vehicles	Evaporative emissions (hydrocarbons and methanol)	• Using methanol 10% blend increased evaporative emissions by 130% for short term use and 220% for long term use.
30	DOE	*	Unleaded gasoline and methanol/indolene mixtures	Auto engines (10)	NO_x, CO, THC, aldehydes, and methanol	• Aldehyde, methanol, and hydrocarbon emissions increased with higher concentration of methanol in the fuel. • CO was reduced by the addition of methanol to the base fuel.
31	DOE	*	10% methanol/90% gasoline blends	Auto engines (7)	NO_x, CO, and evaporative emissions (HC and methanol)	• Data show consistent reduction in CO emissions with use of methanol blends. • Significant increases in evaporative emissions with methanol blends.
32-34	DOE	*	Ethanol, methanol, and gasoline blends	Fleet vehicles	Evaporative and tailpipe hydrocarbon emissions	• 75% increase in evaporative emissions with methanol blends over a straight gasoline. • Emissions were lower for vehicles fueled with gasohol but data was inadequate to conclude a significant difference.
35	DOE	*	Indolene, indolene/methanol blends and ethanol/indolene blends	Pontiac 4-cylinder modified engine	Total aldehydes and specific organics	• Total aldehydes increased 25% in going from indolene to ethanol/indolene and methanol/indolene blends. • Formaldehyde is the largest component of the total aldehydes (up to 90 mole percent of the total).
36	Vulcan Cincinnati	*	No. 6 residual oil, natural gas, and methanol	Small scale boiler test stand and a 49 MW utility boiler	NO_x, CO, and aldehydes	• In the utility boiler, methanol NO_x levels were 7-14% of those measured during residual oil combustion. • CO emission levels of methanol were less than 100 ppm and generally less than those observed for the residual oil. • Aldehyde emissions during methanol combustion were generally less than 1 ppm.
37	Ford Motor Co.	*	Methanol, indonele, and blends	Ford 400 CID engine and 1975 Ford LTD with 400 CID engine	Total hydrocarbons and specific organics	• Methanol/indolene blends gave significantly higher hydrocarbon and aromatic emissions than indolene without a catalyst, but only slightly higher emissions with a catalyst.

(Continued)

TABLE 2. (Continued)

Test No.	Agency	Synfuel	Reference Fuel	Combustion System	Emissions Monitored	General Conclusions
38	DOT	Shale-derived DFM	No. 2 diesel fuel	VW Rabbit engine	NO_x, CO, THC, particulates, Ames test on particulates	• HC and CO emissions were found to be lower and NO_x levels higher for the shale-derived fuel as compared to the petroleum-derived fuel. Particulate emissions were similar for both fuels. • Mutagenic activity of the organics from the particulate matter was similar for the two fuels.
39	Bank of America	*	Methanol/gasoline blends	Fleet vehicles	NO, CO, unburned hydrocarbons	• Blends of 2 to 18% methanol decrease emissions of CO and unburned hydrocarbons and result in improved mileage in new cars. • Certain blends result in operating cost decreases of 1¢/mile.
40	EPA	Shale-derived DFM	No. 2 fuel, and No. 2 fuel with 0.5% nitrogen	Two configurations of a full-scale prototype (25-MW engine-size) gas turbine combustor utilizing a Rich burn/Quick Quench combustor concept	NO_x, CO, unburned hydrocarbons	• Both combustor configurations met program emissions goals using both reference fuels and synfuel. • Unburned HC emissions from one combustor ranged from 0.9 to 7.3 ppmv for No. 2 fuel; 1.1 to 21.8 ppm for No. 2 fuel with 0.5% nitrogen; and 1.3 to 15.3 ppmv for shale-derived DFM at 15% O_2.
41	EPA	SRC-II middle distillate fuel oil and shale-derived residual oil	No. 2 fuel oil and Indonesian/Malaysian residual oil	Prototype full-scale (25-MW engine-size) Rich Burn/Quick Quench gas turbine with two combustor configurations	NO_x, CO, unburned hydrocarbon, and smoke	• All emissions exhaust goals met. • Relationship demonstrated between primary zone residence time and attainable NO_x emission concentrations.
42	EPA	*	Residual and distillate oils, natural gas, propane, isopropanol, methanol	Experimental wall furnace and prototype industrial boiler	NO_x, NO, CO, HC, and aldehydes.	• NO emission levels for the five fuels were as follows: distillate oil > propane > isopropanol > alcohol mixture > methanol. • Although there was considerable scatter in the data, aldehyde concentrations were around 10 ppm for methanol. • NO emissions for all fuels decreased with increasing fraction of flue gas recirculation. • CO and hydrocarbon emissions were always below 50 ppm and smoke was not observed for any fuel.
43	EPA	*	No. 5 residual oil, natural gas, and methanol	Industrial water-tube and fire-tube boilers	NO_x	• Flue gas recirculation was capable of reducing NO_x emissions during methanol combustion. • Methanol NO_x emissions were significantly lower than during residual oil combustion and were also less than during natural gas combustion.
44	EPA	*	Indolene and ethanol blends	Two light duty vehicles	NO_x, CO, THC, ethanol, and evaporative emissions	• The addition of ethanol to indolene reduced tailpipe emissions of THC and CO, but increased NO_x. • Use of gasohol increased evaporative emissions substantially.

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* Because of the unavailability of synfuels, the fuels used in some of these programs were not "true" synfuels (e.g., methanol-derived from natural gas was used instead of coal-derived methanol). These studies, however, are included in this report because they were conducted to show what might be expected from the combustion of actual synfuels in the indicated combustion systems.

TABLE 3. ON-GOING SYNFUEL TESTING PROGRAMS

Sponsoring Agency	Test Fuels	Time Period	Project Description
EPA, Motor Vehicle Emission Laboratory	Shale-derived diesel fuel and SRC-II fuel versus National Average Baseline Diesel Fuel.	1981 to ---	Volkswagen Rabbit diesel engine testing. Emissions monitored to include particulates, NO_x, CO/CO_2, hydrocarbons, and aldehydes.
	Mobil-M gasoline.	1981	Oldsmobile 350 and other engines testing. Emissions monitored include particulates, NO_x, CO/CO_2, and hydrocarbons.
DOE, Bartlesville Energy Technology Center; Contractor/test site:			
A. General Electric, Erie, PA	SRC-II middle distillate and oil shale distillate	1981	Testing of GE EDI-8, 8-cylinder "V" configuration, 5344 cu. in. standing diesel engine for electric power, rail and marine applications. Parameters being evaluated include: starting ability, injection timing, fuel rate variation effects and internal engine temperatures. Emissions monitored include O_2, CO/CO_2, NO_x, SO_2, HC, H_2SO_4 and particulates.
B. Transamerica Delaval, Oakland, CA	SRC-II middle distillate	1981	Testing of Delaval DSR 46, 6-cylinder in-line configuration, 28,600 cu. in. standing diesel engine for electric power, compressor and marine applications. Performance parameters being evaluated include starting ability, precombustion chamber effects, ignition delay, and other engine parameters. To date, the engine has been operated at full load using a pre-mixed blend of 60% SRC-II liquid and 40% diesel oil which had been injected into the combustion chamber with no modification of the engine, followed by increasing proportions of SRC-II liquid up to 100%. Emissions monitored include O_2, CO/CO_2, NO_x, SO_x, THC, and smoke.
C. A.D. Little Beloit, WI	SRC II middle distillate	1981	Fairbank-Morse 38 to 8-1/8, 6-cylinder opposed piston design, 3108 cu. in. standing diesel engine for electric power and marine applications, compressors and pumps being tested. Parameters being evaluated include effects of load variations, combustion pressure vs. time, and engine delay. Emissions monitored include CO/CO_2, NO, NO_2, SO_2, SO_4, HC, PAH, particulates and oxidants.
D. Energy and Environmental Research Springfield, OH	Shale-derived distillate oil and Exxon Donor Solvent coal-derived liquids	1981	Testing of Superior 6-cylinder in line configuration turbo-charged 4120 cu. in. standing diesel engine for use in compressors, pumping and electrical power generation. The purpose of the tests is to compare engine performance parameters during synfuel and conventional fuel combustion. Tests with shale-derived distillate oil and a baseline No. 2 diesel fuel include SASS train sampling for PAH and particulate. Other emissions monitored include CO, HC, NO_x, and smoke. Tests with Exxon Donor Solvent liquids will probably include the above procedures and also pilot injection and pre-injection starting tests.

(Continued)

TABLE 3. (Continued)

Sponsoring Agency	Test Fuels	Time Period	Project Description
E. Acurex Shoreham-by-the-Sea, England	Shale oil residuals.	1981	Testing of A.P.E. Allen BSC 12B 6-cylinder, in-line configuration, 5101 cu. in. standing diesel engine for marine, pumping, compressor and electric power applications. Tests include injection, starting, combustion duration and steadiness. Emissions monitored include CO/CO_2, NO_x, NO_2, THC, and smoke.
DOE, Conservation and Solar Energy Division	Various shale- and coal-derived fuels.	1978-1981	Auto engine dynamometer testing being conducted at SwRI. Particulates, NO_x, CO/CO_2, hydrocarbons, and aldehydes being monitored.
	SRC-II distillates and shale-derived JP-5 and DFM mixed with powdered carbon, sawdust, or other cellulosic material.	1981 to ---	Slurry/fuel project involving diesel engine testing. Particulates, NO_x, and other emissions being monitored.
	Coal-derived methanol and gasohol.	1981 to ---	Testing in 1,000 fleet vehicles; program currently constrained for lack of fuel samples.
DOE, Office of Coal Utilization	SRC-II and shale-derived fuels.	1980 to ---	Medium speed diesel engine testing conducted by SEMT-Pielstich, Paris; Baumester Wain, Copenhagen; Grandi Motori Trieste, Trieste; and Selzer of Switzerland.
	SRC-II middle distillates, a 2.9 to 1 blend of SRC-II middle and heavy distillate, and shale-derived fuels.	1980 to ---	Program conducted at Norwegian Technical Institute in various ships.
	SRC-II middle distillate.	1981 to ---	Continuation of low NO_x fuel combustor concept program (see TTM 32-36). Several combustors to be tested by Westinghouse; staged combustor to be tested at several operating loads at Detroit Diesel Allison; testing of 5 combustors planned at GE.
DOE, Pittsburgh Energy Technology Center	Biomass Fuel, H-Coal, Exxon Donor Solvent, and shale fuel oils.	1981 to October 1982	Continuation of small scale combustion of synthetic fuels program (see Test 28). A 20-hp firetube boiler is to be tested with the above synfuels using No. 2 and No. 6 fuel oils as a baseline. The purpose of the program is to assess the possible environmental impact of substituting synfuels for petroleum in utility and industrial boilers.
Department of Transportation and Rutgers University	Coal- and shale-derived diesel fuel.	1981 to 1982	Testing of a recently-designed and constructed one cylinder diesel engine, including collection of particulates and other combustion products.
Sandia Laboratories	Petroleum-derived synfuel simulation fuels, with higher hydrocarbon/aromatic content than conventional fuels.	1981 to ---	Testing being conducted in single cylinder diesel systems and auto/truck engines from Cummins Engine Co. Emphasis on measurement of flame fronts and other engine/burn parameters. Limited emissions monitoring performed.
Bank of America	Methanol/gasoline blends.	1980 to ---	Testing being conducted in blends ranging from 2 to 18% methanol in fleet vehicles, with emphasis on blends of 2 and 4%. CO, NO, and unburned hydrocarbons being monitored.

TABLE 4. TENTATIVE SYNFUEL TESTING PROGRAMS

Sponsoring Agency	Fuels to be Tested	Time Period	Project Description
Army, MERADCOM, Ft. Belvoir, VA	Diesel fuels and other synfuels (high aromatic content fuels, low lubricity fuels).	1982 to ---	Development of accelerated fuel qualification test procedures, including matrix of specific Army equipment components and candidate fuels; project is part of Army Alternative Fuels Program.
Air Force/Navy/EPA (Under the direction of Capt. H. Cewell, USAF Civil Engineering and Services Center, Tindall AFB)	Shale-derived JP-4, JP-5, and JP-8.	Late 1981	Collection of particulates from various engine combustion tests for toxicity and biological effects testing.
Navy Air Propulsion Test Center (NAVSSES), Trenton, NJ	Various shale-derived fuels.	Pending receipt of synfuel samples	Testing of synfuels in various test burners and aviation equipment.
AF Wright Aeronautical Lab, Aero Propulsion Laboratory, Wright-Patterson AFB, Cincinnati	Various shale-derived fuels.	1982-1983	Engine augmenter tests and whole engine tests on 3 engines; emissions monitoring for NO_x, CO/CO_2, and hydrocarbons.
EPRI	Various liquid and solid synfuels, including shale-derived heavy and middle residuals, and methanol	1981-1986	Testing of synfuels in various diesel engines, turbines, and boilers; limited emissions monitoring for SO_x, NO_x, CO/CO_2, O_2 and/or particulates.
EPA, Motor Vehicle Emission Laboratory	EDS and H-coal liquids	Late 1981 to September 1982	Large standing diesel engines and a GE research engine, using same contractors as on-going programs (see Table 3). Particulate matter to be collected.
	SRC-II fuel	1982	Electronically controlled internal combustion engine at UTC, East Hartford, CT. Limited emissions monitoring.
EPA, Industrial Environmental Research Laboratory, RTP, N.C.	Coal-derived middle and heavy distillates; shale-derived No. 2 fuel oil, methanol (technical grade); and petroleum reference fuels	1981-1982 (Phase I)	Comparative synfuel/petrofuel combustion testing in a 2.5 MM Btu/hr packaged boiler and in a 165 kw stationary diesel to identify conditions leading to major differences in emissions, and to develop recommendations for comparative testing.

the following are some general observations on the status, nature, and thrust of the synfuel testing programs:

- Since the primary use of synfuel products is expected to be as combustion fuels, nearly all synfuel end use testing programs have involved evaluation of fuel suitability for use in combustion systems (auto engines, industrial/utility boilers, turbines, etc.).

- Reflecting the developmental status of the synfuel technologies, the thrust of the synfuel testing programs which have been carried out to date has been to assess equipment performance and fuel handling characteristics. Where some emissions monitoring has been conducted, such monitoring efforts have been limited in scope and have primarily emphasized measurements of gross parameters such as particulates, NO_x, SO_x, etc., emissions. The limited scope of the monitoring programs has also been in part due to: (a) an absence of a clear definition of the specific environmental data which would be required on synfuel products by regulatory agencies (e.g., by EPA's Office of Pesticides and Toxic Substances in connection with the Premanufacturing Notification Section of the Toxic Substances Control Act); and (b) lack of a standard protocol for testing for environmental data acquisition.

- Most of the synfuel end use testing programs have been, or are being, conducted/funded by DOD, EPRI, and DOE. The programs of these organizations have, respectively, emphasized use of shale oil products in military aviation and ship equipment; use of coal liquids in boilers; and testing of methanol and methanol-gasoline blends in auto engines and use of coal and shale-derived fuels in stationary diesel engines.

- Many synfuel developers appear to have in-house synfuel testing programs; the emphasis of these programs is primarily on synfuel characterization and not on end use testing. The data generated in these programs are generally considered company proprietary and are not published.

- Nearly all the refined shale oil products which have been used in combustion testing to date have been from the refining of the 100,000 barrels of Paraho shale oil at Sohio's Toledo (Ohio) refinery. Since this refining operation apparently did not involve the use of typical unit operations which would be employed in commercial refining of shale oil, the refined products from this operation are not considered to be representative of products from any future commercial refining of the shale oil.

- To date the synfuel testing effort has been severely curtailed by lack of adequate quantities of fuel for testing. Some of the planned testing programs will utilize shale oil products from the forthcoming refining of 50,000 barrels of shale oil by Union Oil for the Defense Fuel Supply Center.

- Synfuel products (especially the shale-derived materials) which will be marketed in the future will most likely be blends and not 100 percent pure products. The use of 100 percent pure products in the initial synfuel testing programs has been justified on grounds that it would simulate a possible "extreme/worst" case condition (at least from the standpoint of emissions and their environmental implications).

- Although the performance testing is continuing, the limited data which have been gathered to date indicate that the tested synfuels are generally comparable to petrofuels and do not present any unique problems from the standpoint of fuel handling and combustion characteristics. Potential problems with long-term fuel storage stability (observed with certain shale- and petroleum-derived middle distillates) and durability and material compatibility problems (e.g., possible increase in the engine wear with methanol use) are under investigation.

- The very limited data which have been collected on the emission of criteria pollutants (particulates, NO_x, SO_x, etc.) indicate that, except for a higher emission of NO_x with synfuels having a higher content of fuel-bound nitrogen, the emissions of such criteria pollutants are similar for both synfuel and their petrofuel counterparts. For most synfuels, however, no data have been collected on emissions of non-criteria pollutants such as polycyclic organic matter (POM's), primary aromatic amines, nitropyrenes and other organics. There is also very limited data on overall trace element composition of emissions.

ACKNOWLEDGMENTS

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The synfuel end use testing compendium is based on information and documents provided to the study by individuals/organizations engaged in synfuel characterization and end use testing; gratitude is expressed to the supporting individuals/organizations, particularly those in Table 1, to whom the project is deeply indebted.

EXAMPLE DATA SHEET NO. 1

COMBUSTION AND EMISSION CHARACTERISTICS OF COAL-DERIVED LIQUID

1. FUELS TESTED

Synfuels: SRC-II fuel (5 ratios of medium and heavy boiling range components); H-Coal (syncrude mode of operation, full-range distillate); EDS (full-range distillate).

Reference fuel: No. 6 and No. 2 petroleum-derived fuels.

2. TEST EQUIPMENT

An 80-HP firetube boiler system extensively modified to simulate a utility boiler including an indirectly fired air preheater, a scaled-down utility boiler burner, radiation shields to increase the thermal environment in the combustion chamber, and capabilities to implement staged combustion.

3. TEST SITE

KVB Combustion Research Laboratory, Tustin, California.

4. TEST OBJECTIVES

- Develop an understanding of the effect of compositional variations of a particular coal liquid and the resulting effects on the implementation of combustion modifications for pollutant emission reductions;
- Establish an understanding of the difference in the combustion and emission characteristics of coal liquids produced from various processes--specifically the SRC-II Process, the Exxon Donor Solvent Process, and the H-Coal Process;
- Establish a standard test method, using a small-scale facility, to predict the response to changes in operation of smoking tendency, CO, and NO_x. This will be used to differentiate various fuel properties and the performance of each fuel in a large variety of commercial boilers.

5. SPONSORING AGENCY

Electric Power Research Institute (EPRI)
Power Generation Program
Advanced Power Systems Division
Palo Alto, California

EPRI Project Manager: W.C. Rovesti
Telephone No: 415-855-2519

6. CONTRACTOR

KVB Inc.
Irvine, California

Principal investigators: L.J. Muzio, J.K. Arand
Telephone No. 714-641-6200

7. TEST CONDITIONS

A systematic set of experiments was conducted which investigated the following variables: excess air with single stage combustion, burner stoichiometry with two-staged combustion, firing rate, air preheat temperature, fuel temperature (viscosity), and atomizer (mechanical, steam).

8. ENVIRONMENTAL MONITORING

O_2, CO_2, CO, NO, SO_2, SO_3, unburned hydrocarbons, smoke number, particulate size distribution.

9. PROJECT STATUS

Completed.

10. RESULTS

Emissions from the various synfuels combustion tests in this program are summarized in Table A. A brief description of other emission test results are shown below.

SRC II

Particle size data indicate that SRC-II fuel blends produced finer-size-distribution particulate than No. 6 oil, the exception being SRC-II heavy distillate component under single-stage combustion. Measured SO_2 emissions were consistent with the fuel sulfur content, with nearly all fuel sulfur emitted as SO_2. An SO_3 concentration of 2 ppm for heavy distillate component was the only SRC-II test detecting this pollutant. Reference fuel No. 6 oil burn test also emitted 2 ppm SO_3. Unburned hydrocarbon concentrations measured for SRC-II combustion tests ranged from 1 to 14 ppm.

H-Coal

Average particle size of particulate matter proved to be less than 0.4 microns. Measured SO_2 emissions were consistent with fuel sulfur content in that the SO_2 emissions were the lowest of all synfuels tested. SO_3 was not detected. Unburned hydrocarbon emissions ranged from 1 to 4 ppm.

EDS

Two particle sizing tests showed the average particle size to be less than 0.4 microns. Measured SO_2 emissions were consistent with the fuel sulfur content. EDS flue gas samples showed no detectable levels of SO_3. Measured unburned hydrocarbon emissions were 1 and 2 ppm.

11. REFERENCE

Muzio, L.J. and J.K. Arand. Combustion and Emission Characteristics of Coal-Derived Liquid Fuels. EPRI AP-1878, Electric Power Research Institute, Palo Alto, Calif., 1981.

TABLE A. SUMMARY OF EMISSIONS

		Single-Stage			Two-Stage (Low O_2)			Two-Stage (High O_2)		
Fuel Type	Fuel Ash Content lb/10^6 Btu	O_2 %	Part. lb/10^6 Btu	NO ppm @ 3% O_2	O_2 %	Part. lb/10^6 Btu	NO ppm @ 3% O_2	O_2 %	Part. lb/10^6 Btu	NO ppm @ 3% O_2
No. 6 oil	0.0045	3.7	0.024	270	3.6	0.037	199	-	-	-
SRC-II 5.75/1	0.0017	3.8	0.014	400	3.2	0.022	303	4.9	0.020	382
SRC-II Medium Distillate	0.0012	4.0	0.011	476	3.1	0.017	307	4.2	0.012	342
SRC-II 2.9/1	0.0041	3.3	0.012	361	2.9	0.015	308	4.5	0.017	371
SRC-II 0.4/1	0.018	3.4	0.031	509	3.3	0.039	279	4.7	0.039	375
SRC-II Heavy Distillate	0.034	3.3 3.8	0.029 0.037	381 392	3.5	0.184	249	4.6	0.090	269
SRC-II Heavy Distillate (210°F Fuel Temperature)	0.034	-	-	-	3.2	0.065	339	-	-	-
H-Coal	0.0095	2.8	0.022	247	3.1	0.037	226	4.95	0.034	202
EDS fuel	0.0045	2.8	0.022	259	3.2	0.0184	270	5.15	0.0154	216

EXAMPLE DATA SHEET NO. 2

EFFECT OF FUEL BOUND NITROGEN ON OXIDES OF NITROGEN EMISSIONS FROM A GAS TURBINE ENGINE

1. FUELS TESTED

Synfuel: JP-5 type fuel derived from crude shale oil.

Reference fuel: JP-5 derived from petroleum.

2. TEST EQUIPMENT

Allison T63-A-5A turboshaft engine (free turbine type used in Army OH-58A and Navy TF-57A helicopters).

3. TEST SITE

Naval Air Propulsion Test Center
Trenton, New Jersey

4. TEST OBJECTIVES

- Confirm the presence of high levels of NO_x in engine exhaust;
- Obtain information on conversion efficiency of fuel bound nitrogen into NO_x;
- Assess the impacts of high nitrogen fuel on meeting pollution control regulations.

5. SPONSORING AGENCY

Deputy Chief of Naval Material (Development)
Department of the Navy
Washington, D.C. 20361

Project Officer: L. Maggitti
Telephone No: 202-545-6700

6. CONTRACTOR

Naval Air Propulsion Center
Fuels and Fluid Systems Division, PE71
Trenton, New Jersey 08628

Authors: A.F. Klarman, A.J. Rollo
Telephone No.: 609-896-5841

7. TEST CONDITIONS

The T63-A-5A engine was installed in a sea level test cell using a three-point mounting system. A flywheel and an Industrial Engineering Water Brake, Type 400, were connected to the engine gearbox assembly at the forward power output pad to absorb the engine power. The brake reaction was measured by a Baldwin load cell. All parameters to determine the engine starting and steady-state performance with the fuels were measured using standard test cell instrumentation. Engine performance data is contained in the reference report.

Fuels of varying nitrogen content were tested in a T63-A-5A engine to measure their effects on exhaust gas emissions. Five test fuels varying in fuel bound nitrogen content from 3 μg (nitrogen)/g (fuel) to 902 μg (nitrogen)/g (fuel) were evaluated. The nitrogen content in the fuel was adjusted by mixing a JP-5 type fuel derived from shale oil (902 μg (nitrogen)/g (fuel)) and regular petroleum JP-5 fuel (3 μg (nitrogen)/g (fuel)).

8. ENVIRONMENTAL MONITORING

Hydrocarbons, carbon dioxide, carbon monoxide, and nitrogen oxides.

9. PROJECT STATUS

Project report completed November 1977. This is part of an ongoing Naval program to evaluate fuel products derived from alternate sources.

10. RESULTS

Table B shows the results of the exhaust gas measurements performed during the test program. Additional results include the following:

- NO_x emissions for the same engine power rating increased with increasing fuel nitrogen content.
- The conversion efficiency of fuel bound nitrogen to NO and NO_x was approximately 45 percent for the test data in which the NO and NO_x values could be accurately measured.
- No significant effects were noted on engine performance or carbon monoxide (CO) and unburned hydrocarbons (HC) emissions due to the presence of high levels of fuel bound nitrogen.
- The use of shale derived JP-5 fuel with a high nitrogen content will make it more difficult to meet the EPA NO_x standards for aircraft gas turbine engines.

11. REFERENCE

Klarman, A.F. and A.J. Rollo. "Effect of Fuel Bound Nitrogen on Oxides of Nitrogen Emission From a Gas Turbine Engine", Naval Air Propulsion Center, Trenton, New Jersey, NAPC-PE-1, November 1977, 32 pp.

TABLE B. EMISSION DATA SUMMARY

Fuel Nitrogen µg/g fuel	Engine Power Rate	CO_2	CO			NO			NO_x (as NO_2)			HC			F/A (calculated)
			ppm	g/s	g/kg fuel	ppm	g/s	g/kg fuel	ppm	g/s	g/kg fuel	ppm	g/s	g/kg fuel	
	IDLE	1.98	1035	0.714	99.2	6.7	0.00495	0.680	6.7	0.00690	1.06	157	0.0503	6.99	0.00979
3	60% NR	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	MIL	3.03	160	0.227	9.25	23.9	0.0416[a]	1.69	23.9	0.0637	2.59	5.6	0.00422	0.173	0.0146
	IDLE	2.08	985	0.692	90.5	7.7	0.00579	0.758	7.3	0.00887	1.16	131	0.0427	5.59	0.0105
47	60% NR	2.43	430	0.482	35.0	12.7	0.0152	1.11	13.1	0.0241	1.75	18.3	0.00952	0.692	0.0119
	MIL	3.03	130	0.207	8.60	26.3	0.0415	1.72	26.3	0.0635	2.64	8.4	0.00621	0.258	0.0146
	IDLE	2.08	1005	0.698	92.3	9.1	0.00677	0.895	9.4	0.0108	1.42	134	0.0433	5.71	0.0105
267	60% NR	2.43	380	0.438	31.0	16.5	0.0204	1.44	16.7	0.0315	2.24	14.5	0.00775	0.549	0.0119
	MIL	3.03	140	0.224	9.26	27.6	0.0473	1.96	27.6	0.0726	3.00	11.1	0.00825	0.341	0.0146
	IDLE	2.10	950	0.688	86.7	11.6	0.00900	1.13	12.3	0.0146	1.85	109.6	0.0368	4.65	0.0106
515	60% NR	2.43	445	0.482	36.2	17.8	0.0206	1.55	18.4	0.0327	2.47	18.6	0.00935	0.702	0.0119
	MIL	3.03	130	0.210	8.60	31.6	0.0547	2.24	31.6	0.0838	3.44	8.7	0.00652	0.267	0.0146
	IDLE	2.10	992	0.710	90.4	14.9	0.0114	1.45	16.0	0.0188	2.39	116	0.0385	4.91	0.0106
902	60% NR	2.43	460	0.500	37.4	22.1	0.0257	1.92	22.5	0.0401	3.01	18.2	0.00918	0.687	0.0119
	MIL	3.03	135	0.218	8.93	35.9	0.0621	2.55	36.3	0.0962	3.95	8.4	0.00629	0.258	0.0146

PB83-128462

COMPARATIVE TESTING OF EMISSIONS FROM COMBUSTION† OF SYNTHETIC AND PETROLEUM FUELS

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EMISSIONS FROM COMBUSTION OF SYNTHETIC FUELS

There are two basic reasons to investigate the emissions from the combustion of coal- and shale-derived synthetic fuels:

- The physical and chemical characteristics of these synfuels will probably be different from the petroleum-based analogs that they will replace or supplement (e.g., by blending); therefore, the emissions from their burning are likely to be different.

- The types and numbers of combustors in which synfuels might be used are very large; therefore, the potential for exposure to their emissions is very great.

These two reasons argue for research and development now, before extensive commercialization of synfuels, on procedures that can be used to test emissions from representative combustors burning prototype synfuels, and petrofuels that they may replace. Once developed, such procedures can be used to determine which synfuel/combustor combinations should be avoided, and which combinations will result in "clean" emissions (perhaps cleaner than from present combustion of petroleum-based fuels, or from future combustion of lower-grade petrofuels).

CHARACTERISTICS OF SYNTHETIC FUELS

Both physical and chemical characteristics of fuels can affect combustion emissions. Physical properties of solid and liquid fuels such as particle size, density, viscosity, and surface tension affect the rate at which the fuel volatizes to a combustible (gaseous) state. Many of the solid and liquid products available to date from U.S. synfuel pilot plants have physical properties that tend to make them volatize less easily than the coal and petroleum-based fuels they may replace.

Generally, the chemical properties of pilot-scale synfuels produced to date have also been of concern relative to petroleum analogs, mainly because of their greater concentration of high-molecular-weight organics. A considerable and growing literature exists on the content of aromatic and substituted aromatic components of coal- and shale-based synthetics (e.g., reference 1). There are, however, many process options for producing clean synfuels such as methanol, or refining crude products to specifications meeting or exceeding those for current petroleum fuels.

There is, therefore, a trade off between cleaning the synthetic product before combustion and burning the fuel cleanly. Aside from consideration of fuel handling and distribution concerns, the degree of need for a clean fuel will depend on the combustion application.

THE POTENTIAL POPULATION OF SYNFUELED COMBUSTORS

Emissions are greatly affected by type of combustor and how well it is being operated. Light oil, wood, and even methane can lead to undesirable emissions if they are burned improperly. Aside from the tens of millions of mobile internal-combustion engines that are candidates for synthetic fuels (or blends with petrofuels), many stationary units in this country are presently fired with oil:

- Thousands of large utility boilers.
- Hundreds of thousands of industrial and commercial boilers.
- Hundreds of thousands of stationary diesel engines.
- Millions of commercial and residential furnaces.

There are certainly examples of both "clean" and "dirty" burning units in each of the above categories. Generally speaking, however, the amount of attention given to the operation of the units decreases from top to bottom of the list. Typical combustion efficiency of units in each of the four categories probably follows the same order.

On the other hand, fuels burned in residential and commercial furnaces are generally lighter and cleaner than those in diesels, which in turn are lighter and cleaner than those burned in industrial boilers. Overall, large utility boilers most frequently burn the heaviest fuels of all.

This apparent inverse relationship between attention to operation and cleanliness of fuel leads us to suspect that the primary categories of concern among stationary sources might be the middle two -- industrial/commercial boilers and stationary diesels. Also, a recently completed study on synfuels uses (reference 2) tends to indicate that these two categories are likely to be among the first stationary sources to use synfuels in commercial quantities.

EPA therefore initiated a research and development program early this year to develop a set of engineering procedures for comparative testing of emissions from combustion of coal- and shale-based liquid synthetics and petroleum-based analogs. It is designed to be a multi-phased program with several iterations of procedure development, followed by combustion tests to hone the procedures. The following sections of this paper describe the current status of the initial work (Phase I) of this program.

EXISTING EMISSIONS DATA

Data on emissions from combustion of synfuels are very limited. Data on combustion products from oil burning, especially organics, are also limited. Whereas emissions of inorganics are fairly predictable as oxidation products of fuel constituents, organic products of incomplete combustion are a different story. The possibilities are virtually limitless and much more difficult to predict; carefully collected empirical data are needed.

Because changes in emissions are of greater concern than absolute emission rates when switching to synthetics, data of greatest value will be comparative data on emissions from a synfuel and its petroleum analog(s), burned in an appropriate combustor at representative operating conditions. One reason is the oft-stated observation that emissions from combustion of currently burned petroleum fuels constitute an accepted baseline. Another reason is that physical, biological, and chemical characteristics of synthetic fuels (and their emissions) will be evolving as the synfuel industry evolves. It will therefore be important to continually combustion-test emerging synthetic fuels to understand the best environmental and economic balance between cleaning these fuels and burning them cleanly.

PROCEDURES FOR COMPARATIVE TESTING OF EMISSIONS

After several months of Phase I of the EPA program, a very preliminary set of procedures has been developed that addresses personnel safety, combustor operation, emissions sampling, and sample analysis. An overview of current thoughts on each of these aspects follows.

PERSONNEL SAFETY

Because of the hazardous nature of some of the fuels, samples, and residues being handled, precautions are being taken to protect technicians, supervisory personnel, and observers. The materials requiring greatest attention are spills of synthetic and heavy petroleum fuels, residues from cleaning the combustor, and the collected samples of combustion products. During combustion runs and combustor cleaning operations, specified disposable protective clothing and cartridge respirators must be used. Personnel involved in sample handling, preparation, and analysis are required to follow standard precautionary laboratory procedures.

COMBUSTOR OPERATION

The following considerations are especially important for development of procedures for comparative testing of synfuel combustion emissions:

- A combustor that is representative of intended uses must be used. This will generally preclude use of laboratory-scale burners, and will often require combustors with substantial fuel feed rates.

- Large quantities of the synfuels to be tested will often not be available. This will dictate relatively short combustion runs.

- Run-to-run cross-contamination of internal combustor surfaces is a potential problem that may confuse emission measurement results. Some method of equipment cleaning between runs needs to be developed.

With these three factors, plus other considerations derived from a knowledge of how combustors and their operation affect emissions, a preliminary set of procedures, summarized below, has been established:

1. Clean combustor surfaces. This step will consist of brushing and vacuuming accessible internal surfaces to remove loose deposits from the previous run. This step also applies to the dilution tunnel discussed later.

2. Burn No. 2 oil. A typical No. 2 fuel oil, available in sufficient quantity to be used as a reference fuel for all runs, will be used for approximately 1 hour to bring the combustor to steady operation and "recondition" the internal surfaces.

3. Burn test fuel. The fuel supply will be switched to the synthetic or petroleum fuel to be tested. Each test burn is expected to last 2 to 6 hours.

4. Shut down the combustor, and repeat cycle. Eventually, it is hoped to be able to complete one run (steps 1-3) per day or four runs per week. It remains to be seen, of course, whether stable operation and repeatable results can be obtained in sizable combustors with such short turnaround time.

The test fuel firing rate will be set at 80% load and the excess air adjusted to achieve 10% opacity or less in the stack gas from the boiler (excess air will generally be in the range 5%-10%). This opacity setting represents energy-efficient operation for oil-fired boilers. It also represents marginal performance from a particle emissions standpoint. Differences between fuels in emissions potential will therefore tend to be accentuated at this setting, which should expedite screening for potential problems.

With some of the cleaner fuels, an opacity as high as 10% may not be attainable. In such situations, an excess air setting of about 5% is planned. If, for some of the heavier fuels, an opacity as low as 10% cannot be maintained at a reasonable excess air setting, control at about 35% excess air is planned.

The diesel engine will be operated at its continuous load setting of 165 kW (80% load). It will be operated at approximately 85% excess air, which is typical for such combustors, and the opacity measured but left to vary from fuel to fuel.

FUEL AND EMISSIONS SAMPLING

As shown on Figure 1, five types of samples are being taken during Phase I of the program. They are, briefly:

1. Fuel samples. Grab samples are taken from fuel storage (most of the fuels for Phase I of the program are stored in drums).

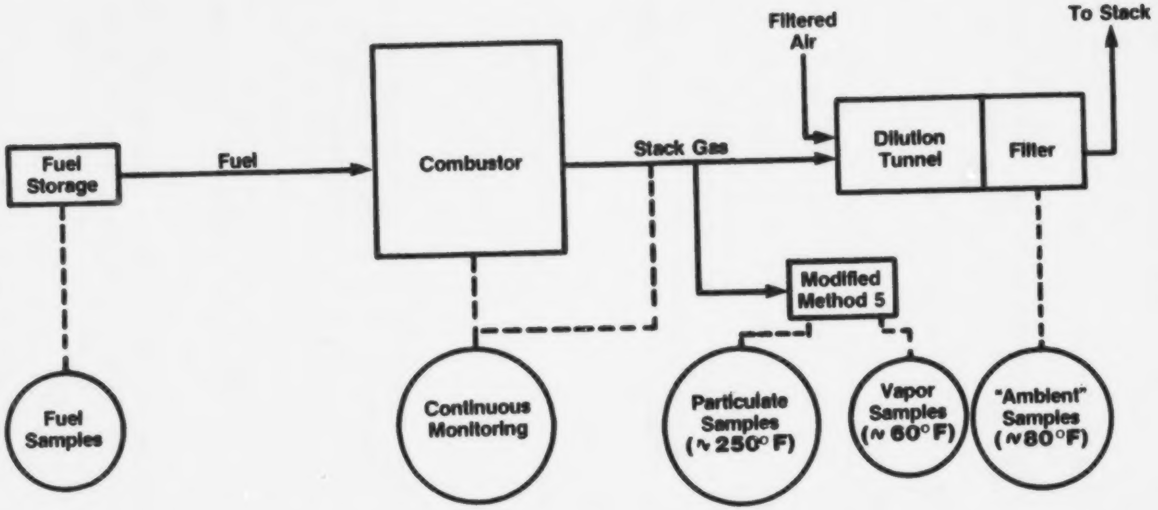

Fuel Storage
Fuel
Combustor
Stack Gas
Filtered Air
Dilution Tunnel
Filter
To Stack
Modified Method 5
Fuel Samples
Continuous Monitoring
Particulate Samples (~250° F)
Vapor Samples (~60° F)
"Ambient" Samples (~80° F)

Figure 1. Sampling - Comparative Emissions Test Procedure (Phase I)

2. Continuous monitoring. Stack gas measurements of O_2, CO, CO_2, NO, NO_2, SO_2, total hydrocarbons, and opacity are made continuously while the conditioning No. 2 fuel and the test fuels are being burned.

3. Particulate samples. Particles in the stack gas will be sampled by a modified Method 5 train (Figure 2 and Reference 3). Particles will be collected in a fiberglass filter at approximately 125°-150°C (250°-300°F) over a 2- to 3-hour period during each run of a test fuel.

4. Vapor samples. Stack gas vapors that pass through the filter of the modified Method 5 train will be cooled to approximately 15°C (60°F) and collected on XAD-2 sorbent material. Vapor samples will be collected over the same periods as the particulate samples.

5. "Ambient" samples. A portion of the stack gas from the combustor will be mixed with filtered air in a dilution tunnel (air-to-stack gas ratio of approximately 10:1). A large (50-cm square) Teflon-coated fiberglass filter at the end of the dilution tunnel will collect particles during the full length of each run of a test fuel.

The dilution tunnel is included in the preliminary procedures for two reasons: (a) by simulating atmospheric dilution/cooling conditions near the exit of the stack, it provides a sample more representative of ambient particles than the ones collected in the stack, and (b) it is an inexpensive way to collect relatively large samples for both chemical and biological testing.

FUEL AND EMISSIONS ANALYSES

Figure 3 summarizes the physical, chemical, and biological analyses being done on the samples of fuels, stack gas particles, stack gas vapors, and simulated "ambient" particles from the dilution tunnel. The primary details of the preliminary analytical procedures follow.

1. Fuel specifications. Standard ASTM procedures are being used to measure the fuel parameters of most common interest to people who purchase or burn fuels. The following measurements are also made for each fuel: inorganic screening by spark source mass spectrometry (SSMS), gas chromatography-mass spectrometry (GC-MS)for qualitative organic screening, spot test for polycyclic aromatic hydrocarbons (PAHs), and boiling point analyses for organics between 100°-300°C and >300°C.

2. Inorganics. Elemental constituents in the fuels will be semi-quantitatively screened by SSMS. Elements selected from the fuel screening will be analyzed in the stack gas and "ambient" particles by atomic absorption (AA).

3. Organics. The objective for analysis of organics, as for inorganics, is to screen for major compositional differences between samples from synthetic fuels and from their petroleum analogs. The battery

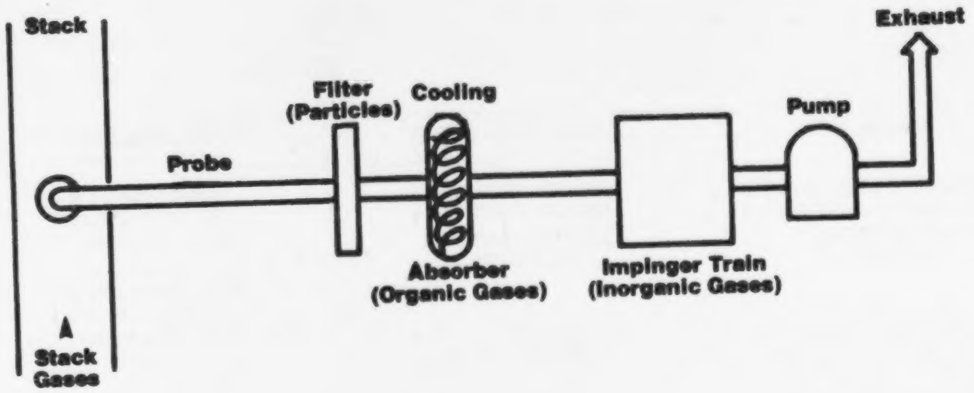
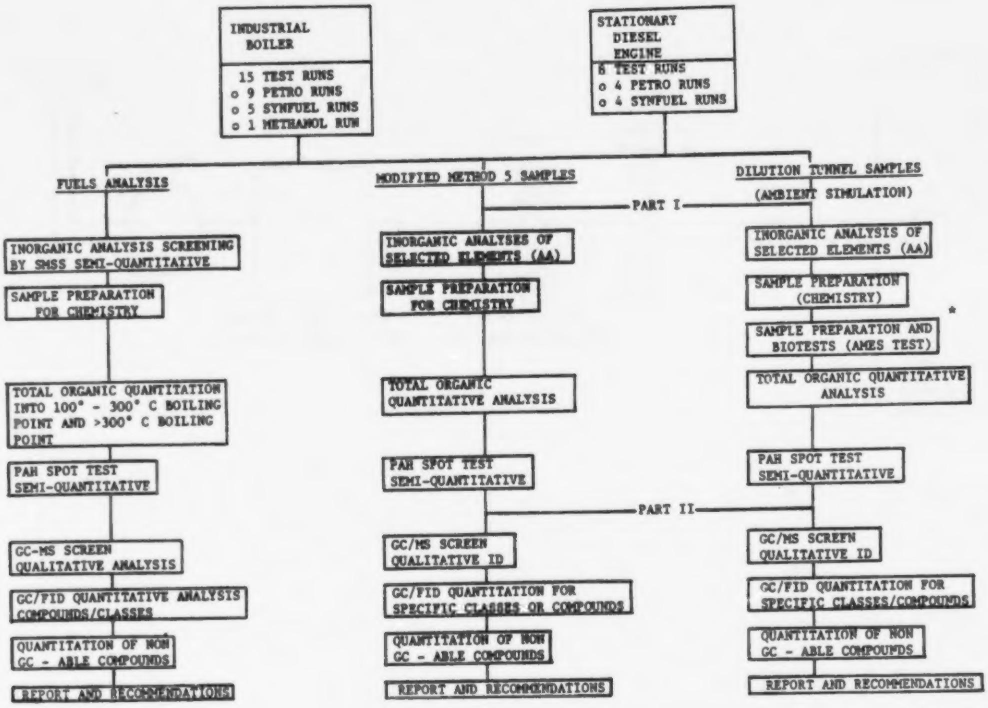

Stack
Exhaust
Filter (Particles)
Cooling
Pump
Probe
Absorber (Organic Gases)
Impinger Train (Inorganic Gases)
Stack Gases

Figure 2. Modified EPA Method 5 Train


INDUSTRIAL BOILER
15 TEST RUNS
o 9 PETRO RUNS
o 5 SYNFUEL RUNS
o 1 METHANOL RUN
STATIONARY DIESEL ENGINE
8 TEST RUNS
o 4 PETRO RUNS
o 4 SYNFUEL RUNS
FUELS ANALYSIS
MODIFIED METHOD 5 SAMPLES
DILUTION TUNNEL SAMPLES
(AMBIENT SIMULATION)
PART I
INORGANIC ANALYSIS SCREENING BY SMSS SEMI-QUANTITATIVE
SAMPLE PREPARATION FOR CHEMISTRY
TOTAL ORGANIC QUANTITATION INTO 100° - 300° C BOILING POINT AND >300° C BOILING POINT
PAH SPOT TEST SEMI-QUANTITATIVE
GC-MS SCREEN QUALITATIVE ANALYSIS
GC/FID QUANTITATIVE ANALYSIS COMPOUNDS/CLASSES
QUANTITATION OF NON GC - ABLE COMPOUNDS
REPORT AND RECOMMENDATIONS
INORGANIC ANALYSES OF SELECTED ELEMENTS (AA)
SAMPLE PREPARATION FOR CHEMISTRY
TOTAL ORGANIC QUANTITATIVE ANALYSIS
PAH SPOT TEST SEMI-QUANTITATIVE
PART II
GC/MS SCREEN QUALITATIVE ID
GC/FID QUANTITATION FOR SPECIFIC CLASSES OR COMPOUNDS
QUANTITATION OF NON GC - ABLE COMPOUNDS
REPORT AND RECOMMENDATIONS
INORGANIC ANALYSIS OF SELECTED ELEMENTS (AA)
SAMPLE PREPARATION (CHEMISTRY)
*
SAMPLE PREPARATION AND BIOTESTS (AMES TEST)
TOTAL ORGANIC QUANTITATIVE ANALYSIS
PAH SPOT TEST SEMI-QUANTITATIVE
GC/MS SCREFN QUALITATIVE ID
GC/FID QUANTITATION FOR SPECIFIC CLASSES/COMPOUNDS
QUANTITATION OF NON GC - ABLE COMPOUNDS
REPORT AND RECOMMENDATIONS

*Bioassay Screening - Based on 200 mg particulate sample (20 mg organic extractables).

Figure 3. Analyses - Comparative Emissions Test Procedure (Phase I)

of techniques includes (a) quantitation of total organics; (b) the "spot" test (reference 4) for PAHs; (c) a qualitative screening by GC-MS, to obtain a very rough "fingerprint" of the organic emissions; and (d) quantitation of the non-gas-chromatographable portion. Samples that are compositionally distinctive, based on the above tests, will be further analyzed by gas chromatography-flame ionization detection (GC-FID) to obtain semi-quantitative information on major classes or compounds present.

All three emissions samples -- stack gas particles, stack gas vapors, and "ambient" particles -- will undergo this battery of tests. The fuels will be analyzed similarly.

4. Bioassays. Comparative biological screening of emission samples in Phase I of the program will be limited to short-term bacterial mutagenicity tests of the type originally developed by Ames. The minimum desirable sample quantity for these tests is 20 mg of organic extractables. If the extractables constitute 10% of the total weight of particles collected, a minimum of 200 mg of particulate catch will be required for the bioassays alone. This amount of sample can only be obtained on the filter at the end of the dilution tunnel, with current procedures. In fact, several of the planned runs with relatively clean fuels are not expected to produce sufficient sample for biological screening. Runs with sufficient sample will be tested using the *Salmonella typhimurium* strain TA98, reverse mutation assay. Each test will be run at 5 to 7 dose levels, both with and without metabolic activation. Any testing beyond this simple assay, such as assays on fractions of samples, will be done only as screening indicates a need and as sample material allows. The need for more extensive biological testing (e.g., additional mutagenesis assays or carcinogenesis assays) in future phases of the program will be determined largely from the results of Phase I.

COMBUSTION EMISSIONS TESTING

A series of comparative combustion emissions tests has been planned as part of Phase I of the program, to evaluate the soundness and practicality of the preliminary testing procedures. The following sections describe the combustors to be used, the fuels to be burned, and the schedule for the remainder of Phase I.

COMBUSTORS

Table 1 lists the characteristics of the two combustors being used at EPA's combustion research facility at the Research Triangle Park, NC. The package boiler (so-called because units of this size can be shop-fabricated and delivered to the site as a "package," rather than being erected at the site) represents small-to-medium-sized fire-tube boilers used in industry and commercial establishments. In addition to its normal dual-fuel burner, it can be (and has been, in past experiments) equipped with a "low-NO_x" burner which promotes staged combustion and lower emissions of NO_x. In Phase I, the conventional burner will be used; in subsequent phases, the effectiveness of the

Table 1. Combustors Being Used in Comparative Emissions Tests (Phase I)

PACKAGE BOILER

- North American scotch marine boiler
- Typical of a broad range of small-to-medium industrial and commercial boilers
- Capacity: 2.5×10^9 kJ/hr fuel rate (2.5×10^6 Btu/hr fuel rate; 2,000 lb/hr steam)
- Operating rate: 80% of capacity; approximately 50 liters per hour (13 gal./hr) of fuel
- Dual-fuel burner (heavy oil and gas)
- Outside dimensions: 1.4 meters (4-1/2 ft) diameter, 3 meters (10 ft) long

STATIONARY DIESEL

- Caterpillar Model D334
- Typical of medium-sized industrial stationary engines
- Capacity: 205 kW (generator output)
- Operating rate: 80% of capacity; approximately 53 liters per hour (14 gal./hr) of fuel

new low-NO_x burner design may be tested on synfuels.

The stationary diesel represents medium-sized industrial and commercial engines used for backup power generation, pumping applications, and powering various other mechanical equipment. Both combustors will be operated as described in the previous section on "Combustor Operation."

Future phases of the program are expected to repeat tests with these combustors for various load and operating settings. In addition, tests may be run with the low-NO_x burner to determine its effect on synfuel combustion emissions. Another possibility is a series of tests on residential furnaces.

FUELS

The fuels used in Phase I testing were chosen to cover a broad range of petroleum and synthetic products. This is mainly to check the applicability of the test procedures. A secondary purpose is to obtain information on major differences in emissions among fuels. It is important to understand that, whereas the coal- and shale-based synthetics being used are typical of those currently available in the U.S. in barrel quantities, they may not be at all typical of synthetics that are eventually marketed for use in industrial boilers and stationary diesels. Therefore, whereas the results from Phase I will be useful in refining the test procedures and planning for Phase II testing, they are not intended for use in environmental assessment of synfuel combustion.

Table 2 lists the fuels being combusted. Additional descriptions follow.

1. Petroleum fuels. Seven petroleum fuels will be tested -- six in the package boiler, and three in the diesel, with two of the seven burned in both units. Four of the fuels will be heavy (No. 6 grade), with sulfur contents ranging from 1 to 3%, nitrogen 0.04 to 0.7%, and ash 0.05 to 0.3%. The other three fuels are lighter (No. 2 grade) with sulfur contents of 0.02 to 0.5%, nitrogen 0.04 to 0.1%, and <0.1% ash. All seven fuels were obtained from east coast distributors.

2. Coal-derived distillates. Three different coal-derived synthetics will be tested. An SRC-II heavy distillate from the Ft. Lewis Solvent Refined Coal pilot plant and an EDS middle distillate from the Exxon Donor Solvent pilot plant in Baytown, Texas, will be burned in the package boiler. The EDS middle distillate and an SRC-II middle distillate will be burned in the stationary diesel.

3. Shale-derived fuel. Refined product (light No. 2) from the Sohio refinery run of Paraho shale oil will be burned in both the package boiler and diesel. This oil has been heavily hydrotreated, and appears to be one of the cleanest fuels to be burned in Phase I.

Future phases of the program are planned to repeat burns with these fuels, other petroleum fuels, other synthetic fuels as they become available, and blends of synthetics and petrofuels.

Table 2. Fuels Being Used in Comparative Emissions Tests (Phase I)

PACKAGE BOILER	RUNS
o 4 Heavy Petroleum Fuels	6
o 2 Light Petroleum Fuels	3
o 1 Coal-Derived Middle Distillate	2
o 1 Coal-Derived Heavy Distillate	2
o 1 Shale-Derived No. 2 Fuel	1
o 1 Methanol	1
	15
STATIONARY DIESEL	
o 3 Light Petroleum Fuels	4
o 2 Coal-Derived Middle Distillates	3
o 1 Shale-Derived No. 2 Fuel	1
	8

Two of the light (No. 2) petroleum fuels, one of the coal-derived middle distillates, and the shale-derived No. 2 fuel are identical for both combustors.

SCHEDULE

The series of combustion emission tests just described will be conducted during November and December of this year. The bulk of the samples will be analyzed from January through March 1982. Data will be compiled and distributed to program participants and fuel suppliers during early spring. A workshop for discussion of data interpretations, test procedure revisions, and plans for Phase II of the program is planned for June 1982. The workshop will bring together EPA and DOE participants, fuel suppliers, and selected additional experts in combustion, analytical chemistry, and data analysis.

SUMMARY

As coal- and shale-derived synthetic fuels begin to enter the market in the 1980s, questions will arise regarding the nature of the emissions from their combustion. A program was recently initiated by EPA to develop engineering procedures for measuring emissions so that concerned parties (EPA, synfuel developers, synfuel users, and others) can address such questions.

The basic approach that has been taken is to compare emissions from synfuels burning to emissions from the burning of petroleum-derived fuels that will be displaced, in combustors that are representative of expected synfuel applications. An important objective of the program is to devise testing procedures that are as simple and inexpensive as possible, but that highlight important differences in emissions from synfuels and petrofuels, where they exist.

The program for development of procedures for making such tests will be multiphased, over a several-year period. Preliminary procedures have been developed for liquid-fueled industrial boilers and stationary diesels. Combustion testing is now underway to check the feasibility and practicality of the procedures. The procedures and data from the first-phase results will be reviewed at a workshop by program participants and additional experts. Subsequent phases of the program will focus on refinement of the procedures and expansion of their applicability to other fuel/combustor combinations.

* * *

Acknowledgements

Many people in the Environmental Protection Agency have been involved in the planning of this program, and many more are expected to contribute as the program matures. The authors especially appreciate the contributions to date of: Michael C. Osborne and Jack H. Wasser of the Combustion Research Branch, Raymond G. Merrill of the Technical Support Staff, and Robert P. Hangebrauck of the Energy Assessment and Control Division, all of the Industrial Environmental Research Laboratory, RTP; Joellen Lewtas of the Health Effects Research Laboratory, RTP; and Donald Barnes and Carl Mazza of the Office of Toxic Substances.

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UNPRESENTED PAPERS

PB83-128470

PROBLEMS ASSOCIATED WITH THE ANALYSIS OF SYNFUELS † PRODUCT, PROCESS, AND WASTEWATER STREAMS

by: H. C. Higman, D. K. Rohrbaugh,
R. H. Colleton, and R. A. Auel
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ABSTRACT

Hittman Associates, Inc., as part of an environmental assessment of coal liquefaction technology sponsored by the U.S. Environmental Protection Agency (EPA), performed various analyses on samples from the Solvent Refined Coal II (SRC-II) plant in Ft. Lewis, Washington, and the Exxon Donor Solvent Plant (EDS) plant in Baytown, Texas. This paper describes several of the problems encountered in these analyses and methods taken to mitigate them. Recommendations are made on approaches for avoiding such problems.

INTRODUCTION

Though there exist standard methodologies for the analysis of pure organic extracts, the complex nature of the product and process streams from synfuels plants cause specific problems which are often complicated by the analytical requirements of the particular study. This paper addresses several problems encountered in the analyses of samples from the SRC-II pilot plant in Ft. Lewis, Washington, and the EDS facility in Baytown, Texas: (1) the analysis of products and effluents to determine process variability over a finite time period; (2) the analysis of volatile organic compounds from heavily loaded sample matrices; (3) the analysis of phenolics from heavily loaded phenolic streams; and (4) the analysis of sulfides, cyanide, thiosulfates, and thiocyanates from heavily loaded aqueous streams.

PROBLEM AREAS

REPRODUCIBILITY IN PROCESS VARIABILITY STUDIES

It is necessary to use a consistent approach in analyzing samples for process variability. For the Ft. Lewis effort, two sets of two samples of a heavy distillate stream were obtained over a 3-day period. This procedure provided a set of 12 discrete samples for studying process variability with built-in controls for sampling and analytical variability.

The heavy distillate stream is a very complex sample matrix containing several hundred discrete components which range in concentration from the parts-per-billion level to several percent of the overall mixture. Analytical options included: (1) several types of fractionation procedures such as the Level 1 Assessment protocol, which yields seven discrete fractions from a silicic acid column; (2) fractionation by Florisil chromatography followed by chemical and further column separation to achieve separations by class for sulfur, nitrogen, and polycyclic aromatic hydrocarbons; and (3) analysis of the gross mixture for major constituents. To eliminate variations which would be introduced by fractionation and concentration procedures, it was decided to analyze the gross mixtures and to use the data obtained to define process, sampling, and analytical variability.

With mixtures of this complexity, capillary gas chromatography provides the most effective separation. It can be coupled with mass spectrometry to obtain as much qualitative information as possible about the major constituents of the mixture. Figure 1 shows the region of the total ion reconstructed chromatogram of a typical sample from the heavy distillate series. The broad peaks are not a function of poor chromatography but, rather, indicate co-eluting components. Several of the major components are identified.

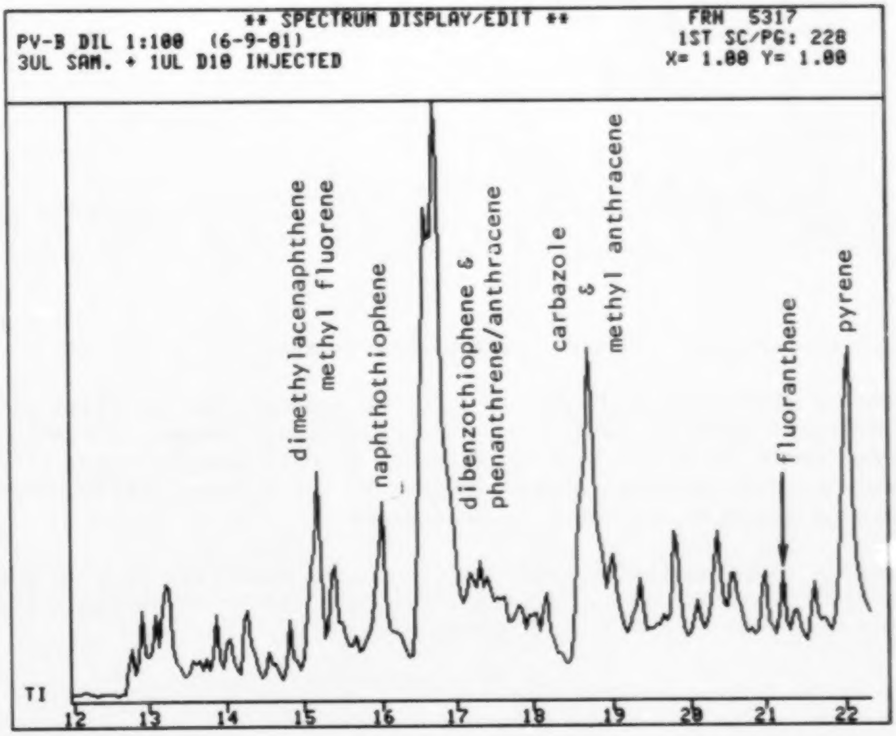

Figure 1. Total Ion Reconstructed Chromatogram of Heavy Distillate Sample from SRC Pilot Plant.

Figure 2 shows four separate total ion chromatograms of different samples taken the same day. The run-to-run reproducibility of these samples is good and can be used effectively for comparison purposes.

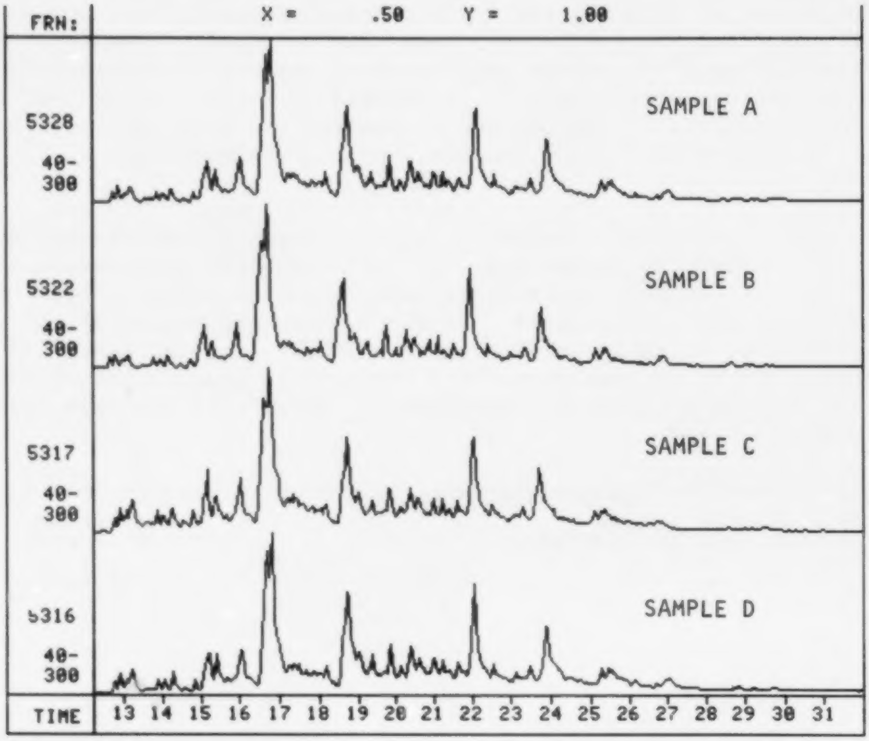

Figure 2. Comparison of Process Variability Samples.

Figure 3 shows selected extracted ion chromatographic profiles (EICP) of the molecular ions for naphthothiophene, dibenzothiophene, phenanthrene/anthracene, and a series of C_2 biphenyls and acenaphthenes. Using EICP, it is possible to discriminate between species in the mixture, while components co-elute when gas chromatography is used alone.

Figure 4 shows another example of co-eluting species. In this case, pyrene and fluoranthene co-elute with substituted phenanthrene/anthracene components and with a series of C_2 carbazoles.

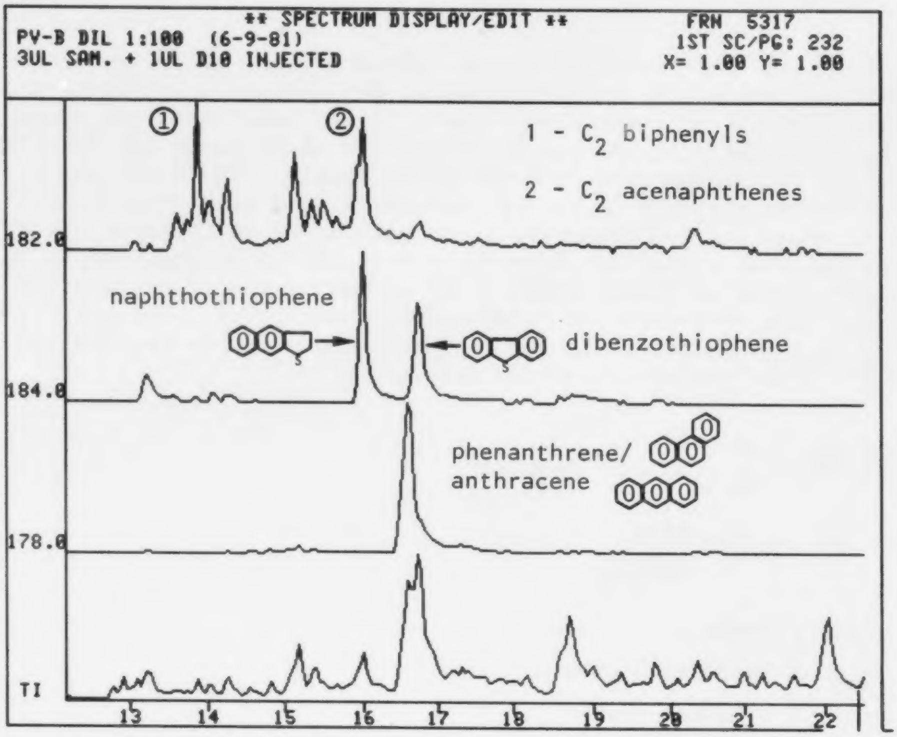

Figure 3. Co-eluting Components in the Anthracene Region

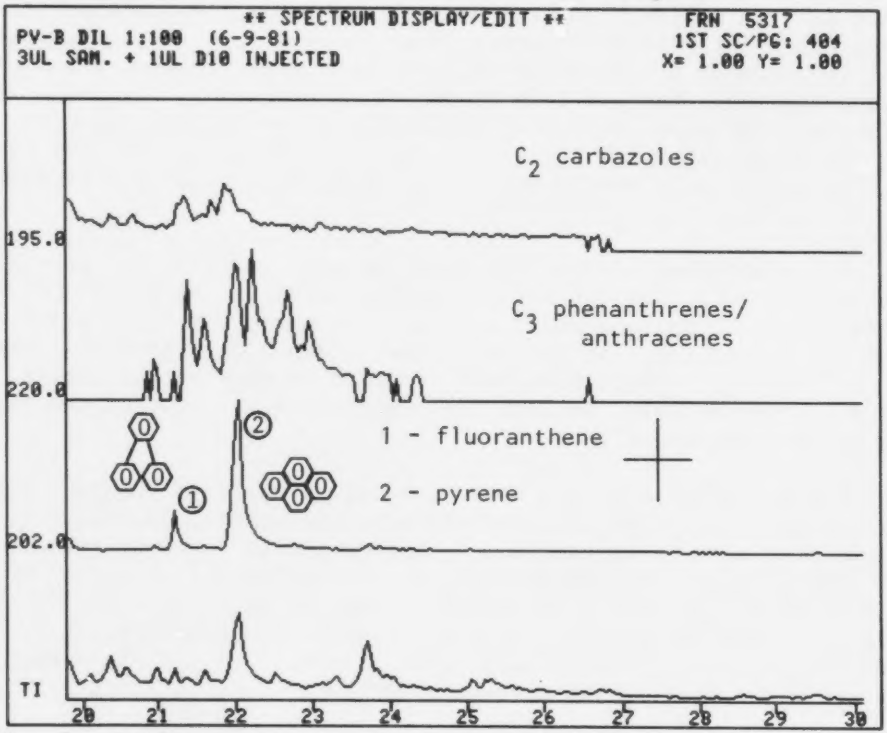

Figure 4. Co-eluting components in the Pyrene Region

By using the extracted ion chromatographic profiles for various components and analyzing the mass spectral data, it is possible to identify a discrete set of components. The areas of peaks from the extracted ion chromatographic profiles can be integrated to generate quantitative data for specific components from the gross sample. The most commonly used calculation involves obtaining integrated peak areas from known amounts of standards and comparing these peak areas to those of a known amount of internal standard. From these data, it is possible to calculate the relative response factor (RRF). The amount of specific components present can then be determined using the equation below. For gas chromatography, this is an excellent and extremely reproducible calculation because the detectors used are very stable.

$$\text{RRF} = \frac{\text{amount } d_{10}}{\text{amount Std.}} \times \frac{\text{Area Std.}}{\text{Area } d_{10}}$$

$$\text{Amount X} = \frac{\text{Area}_x}{\text{Area } d_{10}} \times 1/\text{RRF} \times \text{D}$$

Where: Std. = compound of interest

d_{10} = internal standard

D = dilution factor

When used in conjunction with mass spectrometry, this method yields acceptable reproducibility. However, mass spectrometry is not as stable a detector and is more sensitive to changes in relative concentration of the sample and internal standard than is gas chromatography. This means that RRF values must be calculated very frequently if acceptable quantitative data are to be obtained for repetitive studies. Additionally, the overall sensitivity of the mass spectrometer can change dramatically over short periods of time.

The RRF method was used to generate the data in Table 1. Several representative concentrations for components found in the heavy distillates are shown. Samples A and B are one pair and C and D are a second pair. A and B were taken at the same time, C and D at different times, during the same day. These data were obtained as part of the process variability study and are, we feel, representative in light of the complexity of the sample matrix.

The values in Table 2 were derived by using the data obtained for standards normally used in the generation of RRF values. In this case, these data were used to calculate a working standard curve by least squares linear regression (LSLR) analysis. A second set of least squares linear regression lines were calculated using the data but normalizing the output of the internal standard to a set figure and adjusting the areas of the known compounds to reflect this normalization. All of the lines used had a correlation coefficient exceeding the 95 percent confidence level.

Generally, the values obtained for analytical pairs are in better agreement for the normalized lines.

TABLE 1. COMPARISON OF VALUES OBTAINED BY RRF CALCULATION (g/kg)

	Sample		Sample	
Component	A	B	C	D
Fluorene	2.17	2.36	2.12	1.50
Carbazole	5.67	6.67	7.55	5.68
Dibenzothiophene	8.46	8.96	9.20	8.36
Phenanthrene/Anthracene	20.02	22.64	24.46	20.88
Pyrene	11.66	13.68	13.28	11.37
Chrysene	1.09	1.57	1.73	1.21
Benzo(a)Pyrene/Benzo(e)Pyrene [B(a)P + B(e)P]	.83	.56	.85	.38

TABLE 2. COMPARISON OF SAMPLES BY LSLR AND NORMALIZED LSLR

	LSLR		LSLR-N		LSLR		LSLR-N	
Component	A	B	A	B	C	D	C	D
Fluorene	2.04	1.81	1.74	1.89	1.23	1.07	1.44	1.21
Carbazole	4.95	4.68	4.48	5.27	4.47	3.40	5.59	4.48
Dibenzothiophene	7.27	6.20	6.67	7.06	5.42	4.90	7.25	6.59
Phenanthrene/ Anthracene	16.99	15.41	15.27	17.27	13.15	11.96	16.56	15.93
Pyrene	13.27	12.47	14.8	17.39	9.58	8.69	15.08	14.42
Chrysene	1.32	1.49	1.09	1.58	1.28	1.04	1.44	1.22
B(a)P + B(e)P	.40	.49	.31	.47	.52	.34	.48	.34

Table 3 shows a comparison of the three methods used for quantitation of these selected compounds. The values shown represent a percentage variation from an average value for the paired samples. Using the LSLR data does little to alter the measurements obtained by RRF values when the data are very close, as in the A-B pair for fluorene and in the dibenzothiophene pairs. However, for data which show large variations by the RRF method, such as chrysene and B(a)P+B(e)P, the data obtained by LSLR analysis are more precise. Overall, for the full set of reported components (40-50 in all), the normalized LSLR data sets proved to be more precise. It is our experience that the use of normalized least square linear regression analysis for measurements requiring higher precision than a normal screening technique is a useful alternative to standard procedures. The data from screening analyses could also be calculated by this type of analysis to afford more consistent results.

TABLE 3. COMPARISON OF METHODS BY PERCENTAGE DEVIATION FROM AVERAGE

METHOD/SAMPLE

Component	RRF		LSLR		LSLR-N	
	AB	CD	AB	CD	AB	CD
Fluorene	4.4	17.1	5.6	7.0	3.8	8.3
Carbazole	8.1	14.0	2.9	13.0	8.1	11.0
Dibenzothiophene	2.8	4.7	7.8	5.0	2.9	4.77
Phenanthrene/ Anthracene	6.13	7.9	5.1	4.8	6.1	1.9
Pyrene	8	7.78	3.1	4.9	8.0	2.2
Chrysene	18.0	17.6	5.6	10.0	6.4	10
B(a)P + B(e)P	24	39	11	20	9.5	17

INTERVAL BETWEEN COMPONENTS

	RRF	Absolute Difference	LSLR	Absolute Difference	LSLR-N	Absolute Difference
Fluorene	1.50 - 2.36	.86	1.07 - 2.04	.97	1.21 - 1.84	.63
Carbazole	5.67 - 7.55	1.88	3.40 - 4.95	1.55	4.48 - 5.77	1.29
Dibenzothiophene	8.36 - 9.20	.84	4.90 - 7.27	2.37	6.59 - 7.06	.47
Phenanthrene/ Anthracene	20.02 -24.46	4.44	11.96 - 16.99	5.03	15.93 - 17.44	1.51
Pyrene	11.37 - 13.68	2.31	8.69 - 13.27	4.58	14.42 - 17.39	2.97
Chrysene	1.09 - 1.73	.65	1.04 - 1.49	.45	1.09 - 1.59	.50
B(a)P + B(e)P	.38 - .85	.47	.34 - .56	.22	.34 - .59	.25

PURGE AND TRAP ANALYSIS

The next area of difficulty is the analysis of heavily loaded process streams for volatile organics. The major problem associated with these analyses is the limited capacity of the adsorbing material to efficiently adsorb the levels of organic materials present in process streams. The adsorbent used in our synfuels studies was Tenax resin with a capacity to adsorb 1 to 2 percent of the weight of Tenax in the trap. The actual amount of Tenax is generally 0.5 gm or less. A 0.5 to 1.0 percent loading of this material would be equivalent to 2.5 to 5.0 mg capacity. Above this level, the Tenax will hold more material but with a dramatic decrease in trapping efficiency. Table 4 shows data obtained from a heavily loaded process stream from the EDS plant at Baytown, Texas. Samples B_1 through B_5 are the same sample purged at different levels of concentration. Samples A through F are different samples from the same stream.

TABLE 4. COMPARISON OF PURGE AND TRAP DATA BY VOLUME PURGED

Sample	Quantity Purged (mls)	Quantity Calculated (mg/l)	Observed Load on Tenax/(mg)	Actual Load on System (mg)
B_1	0.25	2890	.7	.7
B_2	1.00	2769	2.7	2.7
B_3	2.50	1700	4.3	6.8
B_4	5.00	997	4.5	13.5
B_5	10.00	460	4.6	27.0
A	1.00	2216	2.6	2.6
B	1.00	2805	2.8	2.8
C	1.00	2642	2.6	2.6
D	5.00	1255	6.3	13.0
E	10.00	523	5.2	26.0
F	10.00	508	5.1	26.0

As indicated in Table 4, adsorbing capacity has no real effect for the samples run at 1.0 mls. Above this level, however, the data are affected significantly. It is important to note that although the overall content of purgeable materials is extremely high, they are not readily amenable to analysis by direct aqueous injection because it does not effectively separate the many components present in these samples. Using the mass spectrometer as a detector and injecting even several μl of aqueous material, there are nanogram to low microgram quantities of many of the components. At levels of 2 g/l, only 2 μg/μl are being analyzed by direct injection.

Table 5 shows the results obtained from a naphtha sample, which should contain a very high percentage of purgeable materials. This sample was run as a pure organic. The samples were diluted 1:10 with methanol. Two samples were run with 100 μl of the diluate injected into 10 mls of H_2O. Two samples were run with 50 μl of the diluate injected into a 10 ml aqueous matrix.

TABLE 5. COMPARISON OF PURGE VALUES FOR NAPHTHA

Sample	Analyzed (μl)	Observed Concentration (g/l)	Observed Loading Tenax (mg/l)	Actual Tenax Loading (mg/l)
Naphtha A	10	382	3.82	5.80
Naphtha B	10	297	2.97	5.80
Naphtha C	5	584	2.92	2.92
Naphtha D	5	576	2.86	2.86

The values at a 50 μl injection of a 1:10 aliquot are reasonable for this type of stream, indicating that approximately 75 percent of the components in the naphtha streams are purgeables.

We recommend that internal process streams be run at a volume of 0.25 to 0.50 mls of sample for purge and trap analysis except for those streams for which there is little or no chance that purgeables are present. A second run can then be made after calculation of an effective column loading. Also, we recommend that volatile organic materials such as naphtha streams be run at levels of no more than 50 μl of a 1:10 diluate. Analytical parameters for streams with higher boiling ranges are based on volatile content. Industry literature can be used as a guide for estimating the quantity of samples to be analyzed. For process streams, we have found that sour water streams, including streams from pumps and drums as well as gas scrubber streams, should be regarded as heavily loaded process streams for volatiles.

PHENOLICS ANALYSIS

A third problem in analyzing process streams is the high level of phenolic materials present in sour water streams. Toxic gases evolve during acidification of the aqueous samples. Also, the high levels of phenolics present in extracts tend to create problems when concentrated for analysis by gas chromatography (GC) and gas chromatography/mass spectometry (GC/MS). Very low recovery rates (20 to 40 percent) have been reported in many cases. The more volatile phenols are extremely difficult to recover quantitatively. For this reason, EPA has recommended a colorimetric method for the analysis of steam-distillable phenol. The method is fairly specific for phenol; however, there are other major phenolics present in these streams, such as cresols, xylenols, and trimethyl phenols. These phenols are not quantitatively measured by this method. We have analyzed these streams by direct aqueous injections as well as colorimetric and GC/MS methods.

Table 6 shows a comparison of the results obtained by GC/MS, colorimetric, and direct injection analysis for two streams heavily loaded with phenolics. In both cases, the GC/MS gave lower values than the direct injection GC method. For heavily loaded samples, the GC method has the advantage of allowing analysis in situ with a minimum of sample handling. The only possible alteration to this method would be to carefully acidify to a slightly acid pH (6.0 to 7.0) any samples which were very basic to assure that all phenolics have been analyzed.

TABLE 6. PHENOLICS BY COMPARATIVE METHODS
(mg/l)

	METHOD		
Sample	GC/MS	Colorimetric	Direct Injection
Sample A	3500	2439	11321
Sample B	4300	16024	13131

The method we used was a slight modification of Standard Method 510E from the 14th edition of Standard Methods for the Examination of Water and Wastewater.[1]

ANALYSIS OF THIOCYANATES AND RELATED SPECIES

There are also problems associated with the analysis of sulfide, cyanide, thiosulfate, and thiocyanate (SCN^-) in streams which have a high sulfide and/or H_2S content. These samples were analyzed in accordance with procedures defined in Manual of Methods: Preservation and Analysis of Coal Gasification Wastewater.[2] We found that the precipitation of sulfide from heavily loaded streams as lead sulfide is not easily accomplished and that the precipitations required several days. In addition, cyanide can easily be lost by occlusion during the precipitation. The amounts of lead sulfide were so great that this occlusion is a very real problem. Dilution of the original samples prior to precipitation was not possible because the lower limits of the required analytical range preclude dilution. Another consideration in the cyanide analysis is the equilibrium shown below. It appears that the equilibrium is being forced to the left as sulfur is removed from the system.

$$Pb^{+2} + 2S^{-2} + CN^- \rightleftharpoons SCN^- + PbS\downarrow$$

Theoretically, the analysis of SCN^- should then become an important parameter. However, the same problems occur in this analysis since sulfides must initially be precipitated and there are high levels of lead sulfide present. To date, no adequate solution to this problem has been developed.

CONCLUSION

There is currently no all-encompassing methodology available for the analysis of process, product, and wastewater streams from synthetic fuels plants. Each type of stream and each individual process stream must be handled under conditions which will optimize the value and validity of the data obtained. In our current studies, we are attempting to modify existing procedures, as appropriate, to provide the most effective analytical approach. In particular, we are correlating GC/MS and GC data by utilizing the qualitative data obtained from GC/MS as a guide, then using capillary gas chromatographic data as the eventual quantitative tool. By incorporating the specificity of the mass spectral data, we are better able to quantitate unresolved gas chromatographic peaks. We are also assessing alternatives to existing methodologies of volatile organics analysis to obtain a more consistent approach to the problem of heavily loaded process streams. Finally, we are attempting to modify the precipitation procedures for sulfides to adapt a method which is viable for heavily loaded process streams.

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SOLVENT EXTRACTION PROCESSING
FOR COAL CONVERSION WASTEWATERS

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ABSTRACT

This paper outlines experimental and modeling techniques that are being used to evaluate solvent extraction processing of coal conversion wastewaters. The project includes characterization of organic contaminants in slagging fixed-bed gasification process wastewater, as well as screening studies to evaluate removal efficiencies for these contaminants. Experiments are also in progress to measure distribution coefficients for several solvent types with phenol and representative base- and neutral-fraction aromatic solutes. These experiments are being performed with both clean water and wastewater systems. Results from these experiments are being evaluated in light of three techniques for estimating distribution coefficients: Modified regular solution theory as used in chemical engineering processing, expanded solubility parameter approach as used in liquid-liquid chromatography, and estimation of octanol-water partition coefficient as employed in environmental science. This paper reviews results obtained to date and explains direction for work during the coming year.

INTRODUCTION

Solvent extraction is a candidate treatment process for reducing organic contaminants from coal conversion wastewater. Solvent extraction is especially attractive for treatment of highly contaminated streams where the cost of treatment may be compensated, in whole or in part, by the value of recovered material and by reduction of loadings on downstream wastewater processing units. Solvent extraction may also eliminate the need for additional physicochemical wastewater treatment steps.

Experimental work now in progress is aimed at defining solvent extraction processing characteristics of a slagging fixed-bed coal gasification wastewater. This work includes tests with both wastewater and clean water systems as well as theoretical considerations aimed at development of a model to aid prediction of the fate of organic contaminants during solvent extraction treatment.

SOLVENT EXTRACTION PROCESSING

A typical solvent extraction system is illustrated in Figure 1 (Earhart, et al., 1977), where it is shown that the process is comprised of three basic unit operations: (1) an extractor where wastewater and solvent are mixed and separated, (2) a solvent regenerator where solvent is separated from extracted solutes for reuse, and (3) a solvent recovery step where residual solvent is removed from the treated wastewater.

Solvent extractors may be classified as either stagewise contactors, such as mixer-settlers, or as differential contact extractors, such as a packed column or rotary disk contactor. Solvent regeneration is usually accomplished by distillation, and solvent recovery may be achieved by either stripping or secondary solvent extraction.

Numerous solvents are available for use in solvent extraction systems. Solvents which have been employed for processing phenolic streams include: light aromatic oil mixtures, tricresyl phosphate, n-butyl acetate (NBA), diisopropylether (DIPE), and methylisobutyl ketone (MIBK). When choosing an extraction solvent, two of the most important considerations are high solute distribution coefficient and low aqueous solubility. While aqueous solubility data are available for most solvents, solvent-solute distribution coefficient data are available for relatively few compounds, notably phenol and its derivatives. It is especially noteworthy that there is essentially no solute distribution coefficient data for the variety of base- and neutral-fraction solutes which may exist in a coal conversion wastewater.

The solute distribution coefficient may be defined as either the equilib ram ratio of solute mass concentration (C, mg/l) in solvent and water phases (K_D'), or as the ratio of solute mole fraction activity coefficients (γ) in each phase (K_D);

$$K_D' = Cs/Cw$$

$$K_D = \gamma_w/\gamma_s$$

where the subscript s refers to the solvent phase and w to the water phase. Mass concentration and mole fraction activity distribution coefficients are related by the ratio of water and solvent molar volumes;

$$K_D' = \frac{Vw}{Vs} K_D$$

Usually solute distribution coefficient data must be determined from laboratory testing, and this may be a costly and time consuming task. However,

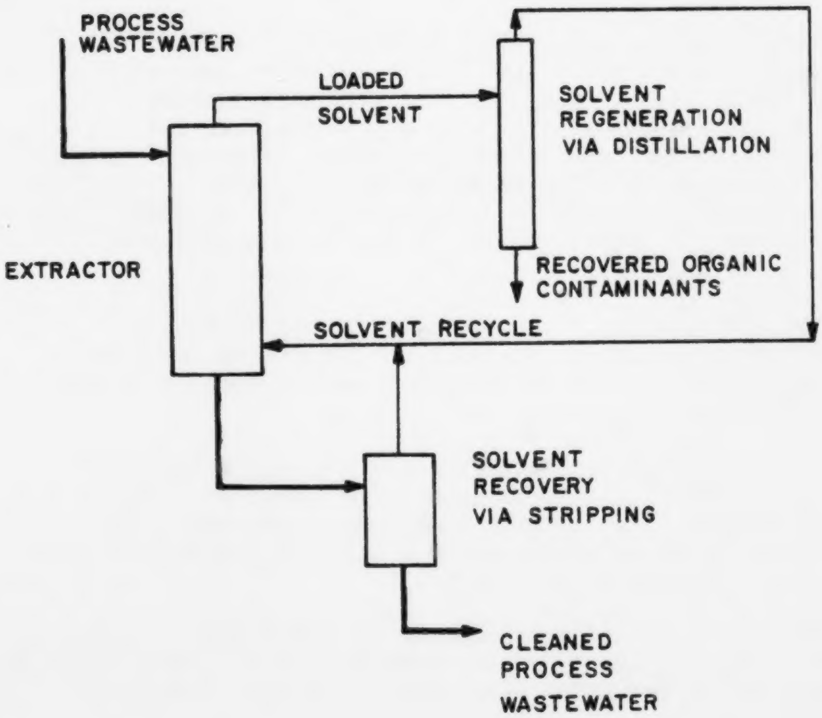
PROCESS WASTEWATER
LOADED SOLVENT
SOLVENT REGENERATION VIA DISTILLATION
EXTRACTOR
RECOVERED ORGANIC CONTAMINANTS
SOLVENT RECYCLE
SOLVENT RECOVERY VIA STRIPPING
CLEANED PROCESS WASTEWATER

FIG. 1 TYPICAL SOLVENT EXTRACTION PROCESS WITH A VOLATILE SOLVENT

time and expense can be saved by using thermodynamic models to estimate solute mole fraction activity distribution coefficients (K_D). Evaluation of the accuracy and applicability of thermodynamic models is included in the theoretical aspects of this project.

PROJECT OBJECTIVES

Work now in progress entails both experimental and theoretical aspects of modeling the fate of organic compounds during wastewater treatment, with emphasis on solvent extraction. Specific objectives of the project are outlined below:

1) Characterize organic contaminates in slagging fixed-bed gasification process wastewater before and after several steps of bench-scale treatment. This work will include screening studies with several solvents to evaluate the efficiency of solvent extraction for removal of phenolics, as well as for removal of base and neutral fraction aromatics. In addition, data from these tests will be used to observe organic specie removal during ammonia stripping and biological oxidation.

2) Review the literature for assessment of models to predict distribution coefficients and compile a listing of the available experimental data on distribution coefficients for wastewater contaminants.

3) Perform experiments to measure distribution coefficients for phenol and representative base and neutral fraction aromatic compounds in both clean water and wastewater systems. The effect of solute concentration on the value of the distribution coefficient will also be evaluated.

4) Assess the applicability and accuracy of distribution coefficient models by comparing model results with experimental data found in this study and experimental data reported in the literature.

RESULTS TO DATE

Several study objectives have been completed or are in the process of being completed. Screening studies have been performed with several solvents to assess their suitability for extraction of phenolic solutes from raw slagging fixed-bed coal gasification wastewater. This wastewater was generated from gasification of a lignite coal.

As a result of these screening studies, MIBK was selected for execution of bench-scale treatment tests incorporating solvent extraction, ammonia stripping and biological oxidation. As a part of this study, organic contaminants were characterized in collaboration with Argonne National Laboratory to assess removal of acid, base and neutral fraction solutes following solvent extraction-ammonia stripping and biological oxidation. Results of this work were presented at the 54th Annual Conference of the Water Pollution Control Federation (Luthy, et al., 1981). A summary of this work is provided in Tables 1 and 2.

Table I shows average solvent extraction treatment characteristics for MIBK extracted wastewater. MIBK is particularly effective for removal of phenolics (K_D~100), and the data show that in the process of reducing phenolics to about 5 mg/ℓ there is also substantial reduction of TOC, COD and BOD. Biological oxidation was evaluated by both activated sludge (AS) and powdered activated carbon-activated sludge (PAC-AS) treatment with 5000 mg/ℓ PAC. Both AS and PAC-AS showed good removal of the pollutants shown in Table 1. The biological oxidation studies showed that solvent extracted wastewater was easier to treat via AS in comparison with wastewater not pretreated for reduction of phenolics. Solvent extraction eliminated the requirement for dilution prior to AS and also reduced wastewater foaming during biological treatment. Solvent extraction also resulted in lower mass loading of residual organic material (eg. color, TOC, and COD) in the biological reactor effluent.

GC/MS analysis of acid, base, and neutral fraction organics were performed on raw condensate, solvent extracted-ammonia stripped wastewater, and AS and PAC-AS effluents. HPLC analysis were performed after each treatment step for detection of eleven polycyclic aromatic hydrocarbons. Table 2, which provides a summary of the analytical results, shows that no organic contaminants could be detected in the acid, base, and neutral fraction suspended phase samples of MIBK extracted wastewater. Analysis of solvent extracted-ammonia stripped aqueous phase acid fraction samples showed the presence of residual phenol, cresols, and other acid fraction compounds, while base and neutral fraction species showed mainly low levels of relatively few compounds. Analysis of AS and PAC-AS treated water showed excellent reduction of those few organic compounds which remained after extraction and stripping. These results showed that solvent extraction for reduction of phenolics offers several wastewater processing advantages for treatment of coal conversion condensates.

This work was followed by a preliminary investigation of thermodynamic models for the prediction of solute distribution coefficients between water and an organic solvent for phenol and other aromatic solutes. The results of this work were presented at the Symposium on Water Management and Pollution Control for Coal Gasification and Liquefaction, sponsored by the Division of Environmental Chemistry at the 182nd ACS National Meeting in August (Campbell and Luthy, 1981). This work showed that most of the experimental solvent extraction studies reported in the literature have focused on phenolic compounds. No distribution coefficient data were found for base and neutral fraction solutes with solvents normally used for phenol recovery. Furthermore, no distribution coefficient data was found for tests using actual coal refinery wastewaters.

A review of the chemical engineering and liquid-liquid chromatography literature revealed that solvent extraction models which are used in these disciplines are based on developments evolving from regular solution theory. These concepts have been applied to several solute-solvent systems, and it was found that some empiricism is necessary for estimation of certain thermodynamic

TABLE 1. SLAGGING FIXED-BED WASTEWATER TREATMENT CHARACTERISTICS[1]

Parameter mg/l unless noted	Raw Wastewater RA-52	Solvent Extracted MIBK	Ammonia Stripped	Activated Sludge	PAC/AS
TOC	11,100	1,950	1,380	580	385
COD	32,000	3,900	2,980	1,340	640
BOD	26,000	2,900	1,820	32	30
Phenolics	5,500	5	3	0.1	<0.02
Org-N	115	51	33	10	4
NH_3-N	6,300	4,400	30	84	20
NO_3^--N	<5	<5	<5	40	100
SCN^-	120	110	105	4	<0.5
CN_{tot}^-	1.8	1.5	1.5	1.4	1.3
CN_{amn}^-	0.1	--	0.1	0.1	<0.1
Freon Ext	410	--	10	<5	<5
Alk (as $CaCO_3$)	20,700	16,300	850	175	72
Cond (μmho/cm)	20,000	18,600	1,490	2,230	2,200
Color (Pt-Co units)	500	500	700	500	<20

[1] Reference: Luthy, Stamoudis, Campbell, and Harrison, 1981. Analyses of solvent extracted samples for TOC, COD and BOD were performed after gentle heating to expel residual MIBK.

Table 2

Concentration (μg/l) of Representative Organic Compounds Identified in Slagging Fixed Bed Quench Water at Various Stages of Treatment

Peak Number	Compound Name	Raw Water		MIBK-Stripped		MIBK-AS	MIBK-AS/PAC
		SS	FW	SS	FW	FW	FW
				Acid Fractions			
20	Phenol	15,100	3,080,000	NT	500	10	3
50	Methyphenol	6,300	427,000	NT	100	1	1
80	Methyphenol	16,400	494,000	NT	80	1	1
140	C_2-Phenol	8,890	155,000	NT	50	NT	NT
260	Hydroxindan	340	3,820	NT	40	NT	NT
370	1-Naphthol	250	1,150	NT	40	NT	NT
				Base Fraction			
10	Pyridine	3.9	14,530	NT	NT	NT	0.1
15	Toluene	NT	77	NT	NT	NT	NT
20	Methylpyridine	12	7,120	NT	1.0	NT	NT
140	Aniline	27	6,500	NT	NT	NT	NT
390	Azanaphthalene	450	500	NT	NT	NT	NT
730	Azafluorene	20	15	NT	NT	NT	NT
				Neutral Fraction			
32	Methylcyclohexane, or C_2-cyclopentene	ND	22,750	NT	4230	NT	NT
35	Benzonitrile	ND	2,900	NT	NT	NT	NT
70	Indene	2300	910	NT	NT	NT	NT
125	C_3-Thiazole	ND	ND	NT	31	1.8	2.0
180	Naphthalene	16,300	26,600	NT	NT	NT	NT
330	Indole	150	5,000	NT	NT	NT	NT
380	Biphenyl	1100	ND	NT	NT	NT	NT
460	Acenaphthene	2480	ND	NT	NT	NT	NT
710	Phenanthrene	4680	ND	NT	NT	NT	NT
790	Fluoranthene	1510	ND	NT	NT	NT	NT
810	Pyrene	830	ND	NT	NT	NT	NT

SS, Suspended Solids; FW, Filtered Water; ND, Not Determinable; NT, Not Dectected.

parameters. Despite this limitation, our analysis has shown that for MIBK and water, neutral fraction aromatic solutes are predicted to have distribution coefficients substantially greater than that for phenol. Thus, in the process of reducing phenolics from relatively high concentrations to comparatively low concentrations, it is expected that neutral fraction solutes would be reduced by even greater proportions.

CURRENT AND FUTURE WORK

Recent experimental work has been directed towards measuring distribution coefficients in both clean water and wastewater systems. This work has examined three solutes: phenol as a representative acid fraction solute, and aniline and pyridine as representative base fraction solutes. These compounds comprise the predominate parent chemical species for compounds previously identified in each of these fractions. It is planned to measure distribution coefficients for benzene with several solvents, as benzene is the parent specie for neutral fraction solutes.

Five solvents have been incorporated in these tests, methylisobutyl ketone (MIBK), di-isopropylether (DIPE), n-butyl acetate (NBA), toluene, and tetradecane These compounds are representative of major classes of organic solvents. MIBK is reportedly used in an extraction process licensed by the Chem-Pro Equipment Corp. (Greminger, et al., 1980), while DIPE is employed in the Lurgi Phenolsolvan process. NBA shows a relatively high distribution coefficient for phenol, and it has been proposed for use in dual-solvent extraction systems (Earheart, et al., 1977). Toluene is a component of coal-devired light oil, which was widely used at one time for extraction of phenolics from coke plant ammonia liquor. Tetradecane was included in this study for comparison purposes because it is an alkane, and because crude oil or related compounds are sometimes involved in petroleum refining operations for extraction of phenol from water or for washing phenol from refinery products.

Solvent extraction tests were performed with these solvents and solutes, in single and multiple solute clean water systems as well as in actual wastewater, to investigate potential synergistic/antagonistic effects. The effect of solute concentration was also investigated. The results of this work are being summarized in the form of a technical paper.

It is planned to execute another treatment study using slagging fixed-bed wastewater generated from gasification of another type of coal. Results obtained from this work would be used to verify the previous results, as well as to assess processing differences for a different water-solvent system. The tests would also include detailed wastewater characterization at different levels of phenol removal. These analyses would provide information on whether various contaminants are removed concomitantly in proportion to their respective distribution coefficients.

The latter tests are important from an economic point of view. Goldstein (1981) notes that single stage extraction is less costly than multiple-stage extraction, and that partial phenol recovery may be economically attractive. An 80 percent recovery of 5,500 mg/l phenolics is reported as supplying enough energy in the recovered material to run the extraction process. Goldstein also recommends solvent extraction if phenolic levels are high and if BOD concentrations are greater than 4,000 to 6,000 mg/l.

ADVANTAGES OF SOLVENT EXTRACTION

The economic issues regarding cost of solvent extraction versus reduced cost of additional wastewater treatment are not easily evaluated. However, it is clear that solvent extraction of phenolic condensates is advantageous for numerous reasons. Some of these reasons are outlined below.

(a) Solvent extraction removes most base and neutral fraction solutes. This is significant because many of the toxic or hazardous organic contaminants in coal conversion wastewaters are found in these fractions.

(b) Recovered material may be combusted for heat value, and this heat may be used to drive the extraction process. Properly designed combusters would destroy hazardous organic compounds.

(c) Solvent extraction would remove hazardous organics, and this would reduce or eliminate problems with disposal of hazardous organic sludges formed as a result of wastewater treatment and reuse.

(d) Solvent extraction would reduce or eliminate problems with carry over of volatile aromatic hydrocarbons during sour water treatment.

(e) Extraction removes creosotes, and thus it is likely that most "tar acids" would be removed. This may be particularly important in treatment of coal liquefaction wastewater, where it is believed that acid treatment is required prior to biological oxidation to precipitate tar acids (Drummond, et al., 1981). Solvent extraction may eliminate the need for this step.

(f) Solvent extraction can eliminate the need for dilution prior to biological oxidation. It has been found in various studies that dilution is required when biological oxidation is employed for treatment of heavily contaminated gasification or liquefaction process condensates (Luthy, 1981; Drummond et al., 1981). Our recent work (Luthy, et al., 1981) has shown that dilution was not necessary when treating solvent extracted coal gasification condensate.

(g) Pretreatment by solvent extraction results in lower mass loading of residual organic material (i.e. TOC, COD, and color) in biological reactor effluent. Also, foaming was not a problem when solvent extracted wastewater was subjected to activated sludge treatment.

(h) Since solvent extraction pretreatment can eliminate the need for dilution water as well as result in lower loadings of residual organics, it should benefit any additional treatment required prior to wastewater reuse.

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APPENDIX

Attendees

Allen	Doreen C.	145 Vista Avenue	Pasadena	CA	91106	Aerovironment Inc.
Altschuler	Morris H.	401 M Street, S. W. (RD-681)	Washington	DC	20460	U.S. EPA
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Anderson	Rick	P. O. Box 2511	Houston	TX	77001	Tennessee Gas Transmission Corp.
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Beavers	R. W.	P. O. Box 5888	Denver	CO	80217	Stearns-Roger Engineering Corp.
Bee	Robert W.	20030 Century Boulevard	Germantown	MD	20874	The Aerospace Corporation
Beekley	Pamela	3401 Lagrande Boulevard	Sacramento	CA	95823	Radian Corporation
Bell	Linda R.	Natural Resources Bldg., P&C Staff	Norris	TN	37828	Tennessee Valley Authority
Beltran	Rafael G.	A.A. 4976	Bogota D.E.	COLOMBIA		University of Los Andes
Berkey	Ed	127 Alleyne Drive	Pittsburgh	PA	15215	Synco Consultants Inc.
Beychok	Milton R.	63 Oak Tree Lane	Irvine	CA	92715	Consulting Engineer
Bixel	John C.	P. O. Box 1026	Princeton	NJ	08540	Mobil Research & Development Corp.
Blake	John H.	Fifty Beale Street	San Francisco	CA	94105	Bechtel Group, Inc.
Bolton	Graham	8150 Leesburg Pike, Suite 600	Vienna	VA	22180	International Gas Consultancy Ltd.
Bombaugh	Karl J.	8501 Mo-Pac Blvd., P. O. Box 9948	Austin	TX	78766	Radian Corporation
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Bosman	M.	P. O. Box 19	9700 MA Groningen	NETHERLANDS		N.V. Nederlandse Gasunie
Bradshaw	W. N.	P. O. Box 5888	Denver	CO	80217	Stearns-Roger Engineering Corp.
Brna	Theodore G.	IERL, MD-61	Research Triangle Park	NC	27711	U.S. EPA
Brown	Charles W.	3800 Frederica St.	Owensboro	KY	42301	Texas Gas Transmission Corp.
Brown	Richard D.	1820 Dolley Madison Boulevard	McLean	VA	22102	The MITRE Corporation
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Burton	Ellison S.	3344 Federal, Office of Fossil Energy	Washington	DC	20461	U.S. Department of Energy
Carley	Robert	2420 Alcott Street	Denver	CO	80211	McLaughlin Industrial Waste Engineers
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Chartrand	Dean	15740 Shady Grove Road	Gaithersburg	MD	20877	Bechtel Power Corporation
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Dickert	Charles T.	Independence Mall West	Philadelphia	PA	19105	Rohm and Haas Company
Dounoucos	Angelo	P. O. Box 43, Bldg. 5, Room 425	Schenectady	NY	12301	General Electric Company
Drabkin	Marvin	2100 M Street, N.W., Suite 607	Washington	DC	20586	U.S. Synthetic Fuels Corp.
Drummond	Charles J.	P. O. Box 10940	Pittsburgh	PA	15236	U.S. Department of Energy
Dubberly	Agnes K.	650 South Cherry Street, Suite 400	Denver	CO	80222	Pace Co. Consultants and Engineers
Dunkle	D. M.	115 Gibraltar Road	Horsham	PA	19044	IU Conversion Systems, Inc.
Duprey	Robert L.	1860 Lincoln Street (8AH)	Denver	CO	80295	U.S. EPA, Region VIII
El-Ashry	Mohamed T.		Norris	TN	37828	Tennessee Valley Authority
Elms	Bruce R.	12075 E. 45th Avenue	Denver	CO	80239	Black & Veatch
Ely	Robert B.	9210 South East 68th Street	Mercer Island	WA	98040	Zimpro, Inc.
Engel	Paul	2244 Walnut Grove Ave., Rm. 492	Rosemead	CA	91770	Southern California Edison Company
Englick	Jack	133 S. Van Gordon St., Ste. 206C	Denver	CO	80228	FMC Corporation
Erickson	Ron		Missoula	MT	59812	University of Montana

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Fischer	Marshall	1860 Lincoln Street	Denver	CO	80295	U.S. EPA, Region VIII
Fischer	William H.	P. O. Box 1498	Reading	PA	19607	Gilbert/Commonwealth Assoc.
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Fuchs	Michael R.	8501 Mo-Pac Blvd., P. O. Box 9948	Austin	TX	78766	Radian Corporation
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Geise	Bill	1860 Lincoln Street	Denver	CO	80295	U.S. EPA, Region VIII
Ghassemi	Masood	One Space Park Drive, R4/2150	Redondo Beach	CA	90278	TRW, Inc.
Goldgraben	Gerald	1820 Dolley Madison Boulevard	McLean	VA	22102	The MITRE Corporation
Gorshaw	Cindy	P. O. Box 2309	Englewood	CO	80155	Phillips Petroleum Co.
Granger	Tom	Two World Trade Center, 90th Floor	New York	NY	10048	Envirosphere Co.
Hafker	William R.	P. O. Box 101	Florham Park	NJ	07932	Exxon Research & Engineering Co.
Hale, Jr.	Matthew	401 M Street, S. W. (TS-794)	Washington	DC	20460	U.S. EPA
Hamanishi	Henry	P. O. Box 7808, II M-K Plaza	Boise	ID	83729	Morrison-Knudsen Company, Inc.
Hangebrauck	Robert P.	IERL, MD-61	Research Triangle Park	NC	27711	U.S. EPA
Harlow	George L.	345 Courtland Street	Atlanta	GA	30365	U.S. EPA, Region IV
Hayward, Jr.	James C.	Entex Building, P. O. Box 3105	Houston	TX	77001	Shell Oil Company
Henschel	D. Bruce	IERL, MD-61	Research Triangle Park	NC	27711	U.S. EPA
Higgins	Charles	P. O. Box 806	Franklin	TN	37064	MCI/Consulting Engineers Inc.
Higman	Howard	9190 Red Branch Road	Columbia	MD	21045	Hittman Associates, Inc.
Hoffman	Dale A.	134 Union Boulevard	Lakewood	CO	80225	U.S. Fish & Wildlife Service
Honefenger	Ron L.	P. O. Box 1396	Houston	TX	77251	Transco Companies, Inc.
Honerkamp	Russell L.	8501 Mo-Pac Blvd., P. O. Box 9948	Austin	TX	78766	Radian Corporation
Hoskins	W. W.	700 S. Ash	Denver	CO	80217	Stearns-Roger Engineering Corp.
Hospodarec	Robert W.	3333 Michelson Drive	Irvine	CA	92730	Fluor Engineers & Constructors, Inc.
Howard	F. Sidney	One Davis Drive	Belmont	CA	94002	Lurgi Corp.
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Hughes	W. David	P. O. Box 68, 695 North 7th	Brighton	CO	80601	Century Refining Co.
Hull	Jeane L.	500 Boyd Building, 18th & Carey Ave.	Cheyenne	WY	82002	Wyoming Office of Industrial Siting
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Kamperman	E. F.	P. O. Box 5440	Norwalk	CT	06856	UOP/Air Correction Division
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Kent	Raymond L.	9190 Red Branch Road	Columbia	MD	21045	Hittman Associates, Inc.
Kimura	S. Gene	P. O. Box 43	Schenectady	NY	12301	General Electric Company
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Lethi	Minh-Triet	401 M Street, S. W. (PM-221)	Washington	DC	20460	U.S. EPA
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Long	Dick	1860 Lincoln Street	Denver	CO	80295	U.S. EPA, Region VIII
Longenberger	Fred	1860 Lincoln Street	Denver	CO	80295	U.S. EPA, Region VIII
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Mirchandani	Dilip	Two World Trade Center	New York	NY	10048	Envirosphere Co.
Miullo	Nat	1860 Lincoln Street	Denver	CO	80295	U.S. EPA, Region VIII
Moghissi	A. Alan	401 M Street, S. W. (RD-682)	Washington	DC	20460	U.S. EPA
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Murray, Jr.	Charles F.	One Space Park Drive	Redondo Beach	CA	90278	TRW, Inc.
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Place	Barry G.	P. O. Box 512	Milwaukee	WI	53201	Allis Chalmers
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Raben	Irwin A.	130 Sandringham South	Moraga	CA	94556	IAR Technology Inc.

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Robbins	Steve M.	P. O. Box 3 (04-107)	Houston	TX	77001	Brown & Root, Inc.
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Roosmagi	Carl E.	P. O. Box 3395, University Station	Laramie	WY	82071	Laramie Energy Technology Center
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Rosenfield	Henry	P. O. Box 2521	Houston	TX	77001	Texas Eastern
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Shankland	Bob	1860 Lincoln Street	Denver	CO	80295	U.S. EPA, Region VIII
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Smith	G. Richard	363 South Harlan St., Suite 209	Lakewood	CO	80226	Envirotech Process Equipment
Smith	N. Dean	IERL, MD-61	Research Triangle Park	NC	27711	U.S. EPA
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Soukup	Charles L.		Rothschild	WI	54474	Zimpro, Inc.
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Troscinski	Ed	2901 Butterfield Road	Oak Brook	IL	60521	Nalco Chemical Co.
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